GRAND RAPIDS COMMUNITY COLLEGE: CHM 120 SURVEY OF GENERAL CHEMISTRY

Thomas Neils
Grand Rapids Community College

LibreTexts™

Grand Rapids Community College

Grand Rapids Community College: CHM 120 Survey of General Chemistry

Thomas Neils

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

The LibreTexts mission is to unite students, faculty and scholars in a cooperative effort to develop an easy-to-use online platform for the construction, customization, and dissemination of OER content to reduce the burdens of unreasonable textbook costs to our students and society. The LibreTexts project is a multi-institutional collaborative venture to develop the next generation of open-access texts to improve postsecondary education at all levels of higher learning by developing an Open Access Resource environment. The project currently consists of 14 independently operating and interconnected libraries that are constantly being optimized by students, faculty, and outside experts to supplant conventional paper-based books. These free textbook alternatives are organized within a central environment that is both vertically (from advance to basic level) and horizontally (across different fields) integrated.

The LibreTexts libraries are Powered by NICE CXOne and are supported by the Department of Education Open Textbook Pilot Project, 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. More information on our activities can be found via Facebook (https://facebook.com/Libretexts), Twitter (https://twitter.com/libretexts), or our blog (http://Blog.Libretexts.org).

This text was compiled on 01/06/2025

TABLE OF CONTENTS

1: Matter and Energy

2: Atomic Structure

3: Chemical Formulas and Bonding

4: Intermolecular Forces, Phases, and Solutions

5: The Numbers Game - Solutions and Stoichiometry

6: Reaction Kinetics

7: Equilibrium and Thermodynamics

8: Acids and Bases

9: Electrochemistry

Index

Glossary

Detailed Licensing

Licensing

CHAPTER OVERVIEW

1: Matter and Energy

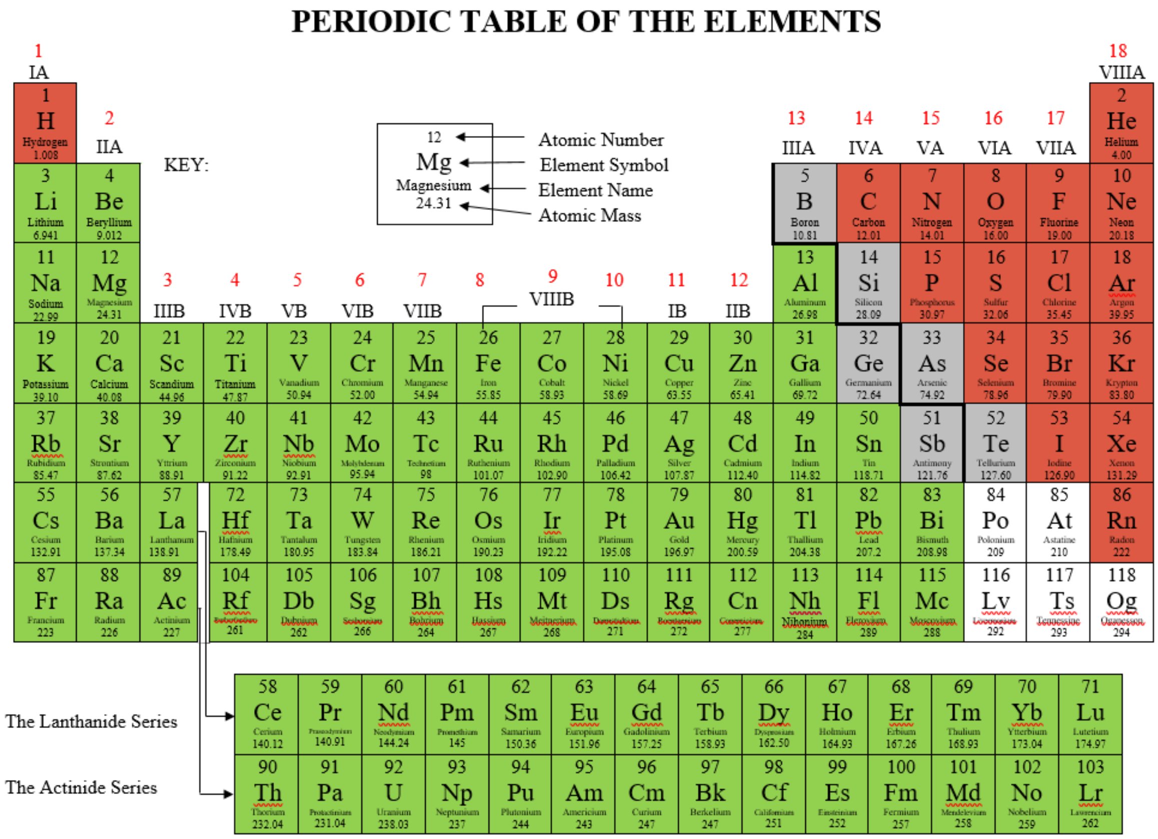
1.1 The Terms of Science

1.2: A First Look at the Periodic Table

Building Blocks

Chemistry involves studying the interaction of the basic building blocks of nature. These building blocks are the atoms of the 118 known elements. People often get confused about atoms and elements. Atoms are the smallest particle of an element that exhibit the properties of that element. An analogy for elements and atoms is Legos^{TM}. Each Lego piece is an atom, and each shape represents an element. Thus, all cube-shaped Lego pieces with one "peg" on top, regardless of color, could represent H atoms, and all rectangular box pieces with two pegs on top, regardless of color, could represent He atoms. In nature, the defining feature of each element is the number of protons in the nucleus, which is called the **atomic number** of that element. Chemists created an organized chart of the elements called the Periodic Table of the Elements. In the most common format of the table, the elements are arranged in order of increasing atomic numbers.

The periodic table is not simply a grid of elements arranged numerically. In the periodic table, the elements are arranged in horizontal rows called periods, and into vertical columns called groups. These groups are numbered by two, somewhat conflicting, schemes. In the simplest presentation, favored by the International Union of Pure and Applied Chemistry (**IUPAC**), the groups are simply numbered 1-18. The convention in much of the world, however, is to number the first two groups IA and IIA, the last six groups IIIA-VIIIA; the middle ten groups are then numbered IB-VIIIB (but not in that order!). While the IUPAC numbering appears much simpler, in this class we will use the "old-fashioned" nomenclature (IA-VIIIA). The reason for this choice will become more apparent in later chapters when we discuss “valence" electrons and bonding. The actual layout of the periodic table is based on the grouping of the elements according to chemical properties. For example, elements in each group of the periodic table (each vertical column) will share many of the same chemical properties. As we discuss the properties of elements and the ways they combine with other elements, the reasons for this particular arrangement of the periodic table will become more obvious.



PERIODIC TABLE OF THE ELEMENTS

KEY:

12	Atomic Number
Mg	Element Symbol
Magnesium	Element Name
24.31	Atomic Mass

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H Hydrogen 1.008																	2 He Helium 4.00
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.41	31 Ga Gallium 69.72	32 Ge Germanium 72.64	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium 98	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.40	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.34	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium 209	85 At Astatine 210	86 Rn Radon 222
87 Fr Francium 223	88 Ra Radium 226	89 Ac Actinium 227	104 Rf Rutherfordium 261	105 Db Dubnium 262	106 Sg Seaborgium 266	107 Bh Bohrium 264	108 Hs Hassium 267	109 Mt Meitnerium 268	110 Ds Darmstadtium 271	111 Rg Roentgenium 272	112 Cn Copernicium 277	113 Nh Nihonium 284	114 Fl Flerovium 289	115 Mc Moscovium 288	116 Lv Livermorium 292	117 Ts Tennessine 293	118 Og Oganesson 294

The Lanthanide Series	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 145	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
The Actinide Series	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237	94 Pu Plutonium 244	95 Am Americium 243	96 Cm Curium 247	97 Bk Berkelium 247	98 Cf Californium 251	99 Es Einsteinium 252	100 Fm Fermium 257	101 Md Mendelevium 258	102 No Nobelium 259	103 Lr Lawrencium 262

As you can see, each element in the periodic table is represented by a box containing the chemical symbol, the atomic number (the number of protons in the nucleus) and the atomic mass of the element. As we will discover, the atomic mass is the weighted average of the masses of all of the natural isotopes of the particular element.

The elements can be classified in many ways. For instance, elements in Groups IA – VIIIA are called the representative, or main group, elements, and the elements in Groups IB - VIIIB are called the transition metals. The broadest classification of elements is into **metals**, **metalloids** (or **semi-metals**) and **nonmetals**. The metallic elements are shown in green on the table here. Metals are solids at room temperature (except for mercury), can conduct electricity, and are usually malleable (can be rolled into sheets) and ductile (can be drawn into wires). Metals are usually separated into the main group metals in Groups IA - VA and the transition metals in Groups IB - VIIIB. Nonmetals (red in the figure) do not conduct electricity well or at all, and have a variety of physical states (some are solids, some liquids and some gases). At the border between metals and nonmetals lie the elements boron, silicon, germanium, arsenic, antimony and tellurium. These elements share physical properties of metals and nonmetals and are called metalloids, or semi-metals. The common semiconductors silicon and germanium are in this group, and it is their unique electrical properties that make transistors and other solid-state devices possible. The elements Po, At, Lv, Ts, and Og are all fairly rare elements, and there is some discussion about how they should be classified. We will not concern ourselves with them.

Named Families

Group IA: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. The name "alkali" comes from an Arabic term related to ashes from burned plants. These ashes contain large amounts of potassium and sodium compounds that form basic aqueous solutions. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth’s crust, respectively. **Note**: Hydrogen is generally placed in Group 1, but it is **not** an alkali metal.

Group IIA: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. The name "alkaline earth" comes from the fact that the oxides of the metals in this family were called "earths", and when these compounds are placed in water, the solution becomes basic. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group VIIA: The Halogens

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

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

Group VIIIA: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, radon, and oganesson. Because the noble gases are composed of only single atoms, they are called monatomic elements. At room temperature and pressure, they are unreactive gases. This lack of reactivity led to their name, in that "noble" elements would not interact with the rest of the elements. Because of their lack of reactivity, for many years they were also called inert gases or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

Contributors

- Paul R. Young, Professor of Chemistry, University of Illinois at Chicago, Wiki: AskTheNerd; PRY@askthenerd.com - pyoung@uic.edu; ChemistryOnline.com
- Tom Neils (Grand Rapids Community College)

Template:HideTOC

1.3: The Classification of Matter

Skills to Develop

- To classify matter.

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

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

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

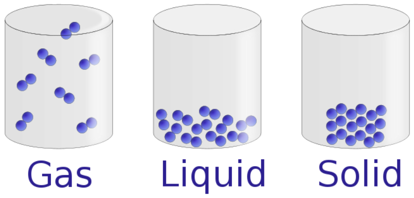


***Figure* 1.3.1** *: The Three States of Matter. Solids have a defined shape and volume. Liquids have a fixed volume but flow to assume the shape of their containers. Gases completely fill their containers, regardless of volume. Figure used with permission from Wikipedia*

Pure Substances and Mixtures

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

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

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

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

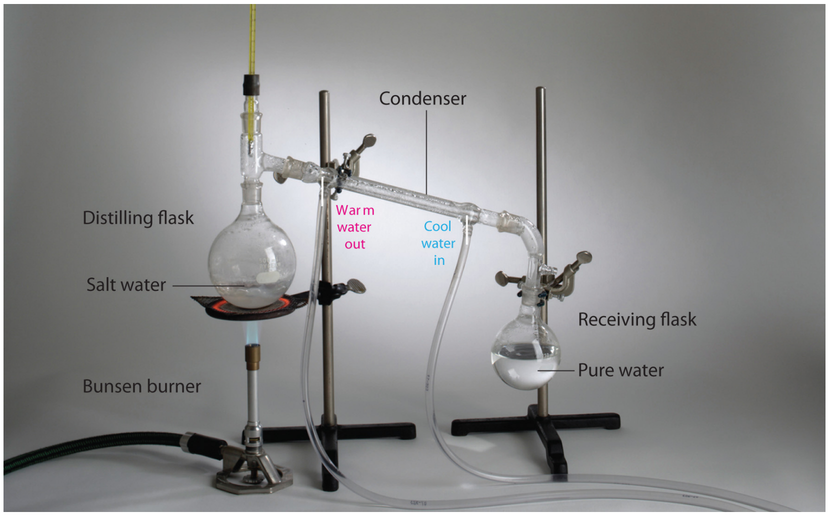


Figure 1.3.3: *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the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

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

Crystallization separates mixtures based on differences in solubility, a measure of how much solid substance remains dissolved in a given amount of a specified liquid. Most substances are more soluble at higher temperatures, so a mixture of two or more substances can be dissolved at an elevated temperature and then allowed to cool slowly. Alternatively, the liquid, called the solvent, may be allowed to evaporate. In either case, the least soluble of the dissolved substances, the one that is least likely to remain in solution, usually forms crystals first, and these crystals can be removed from the remaining solution by filtration.

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

Most mixtures can be separated into pure substances, which may be either elements or compounds. An **element**, such as gray, metallic sodium, is a substance that cannot be broken down into simpler ones by chemical changes; a **compound**, such as white, crystalline sodium chloride, contains atoms of two or more elements that have been chemically combined, and has chemical and physical properties that are usually different from those of the elements of which it is composed. With only a few exceptions, a particular compound has the same elemental composition (the same elements in the same proportions) regardless of its source or history. The chemical composition of a substance is altered in a process called a **chemical change**. The conversion of two or more elements, such as sodium and chlorine, to a chemical compound, sodium chloride, is an example of a chemical change, often called a chemical reaction. Currently, about 118 elements are known, but millions of chemical compounds have been prepared from these 118 elements. The known elements are listed in the periodic table.

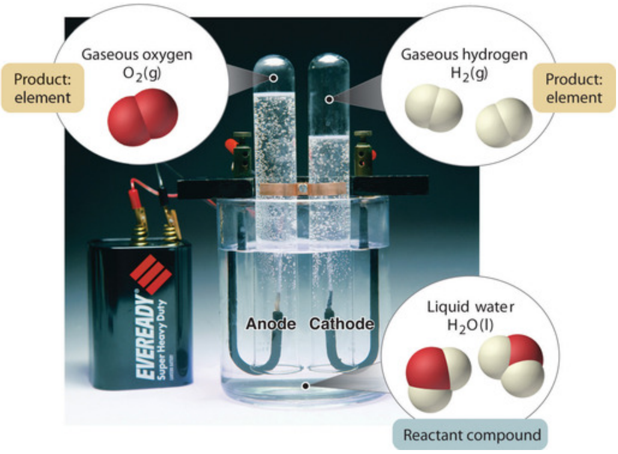


Figure* $1.3.5$*: The Decomposition of Water to Hydrogen and Oxygen by Electrolysis. Water is a chemical compound; hydrogen and oxygen are elements.

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

The overall organization of matter and the methods used to separate mixtures are summarized in Figure $1.3.6$.

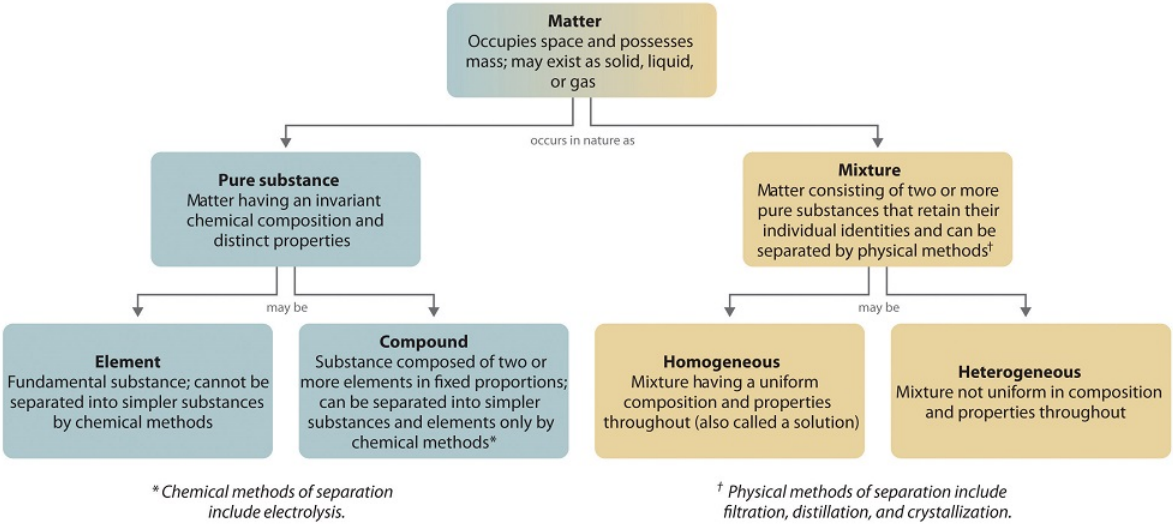


Figure* $1.3.6$*: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Example 1.3.1

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

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

Given: a chemical substance

Asked for: its classification

Strategy:

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

Solution:

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

Exercise 1.3.1

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

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer A

solution

Answer B

element

Answer C

heterogeneous mixture

Answer D

compound

Physical versus Chemical Properties

The characteristics that enable us to distinguish one substance from another are called properties. A physical property is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A physical change is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water ***Figure* $1.3.7$**. Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.

***Figure* $1.3.7$:** *(a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr).*

The change of one type of matter into another type (or the inability to change) is a chemical property. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize ***Figure* $1.3.8$**. Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.


(a) (b)

***Figure Figure* $1.3.8$*:** *(a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)*

To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting ***Figure*** $1.3.9$.

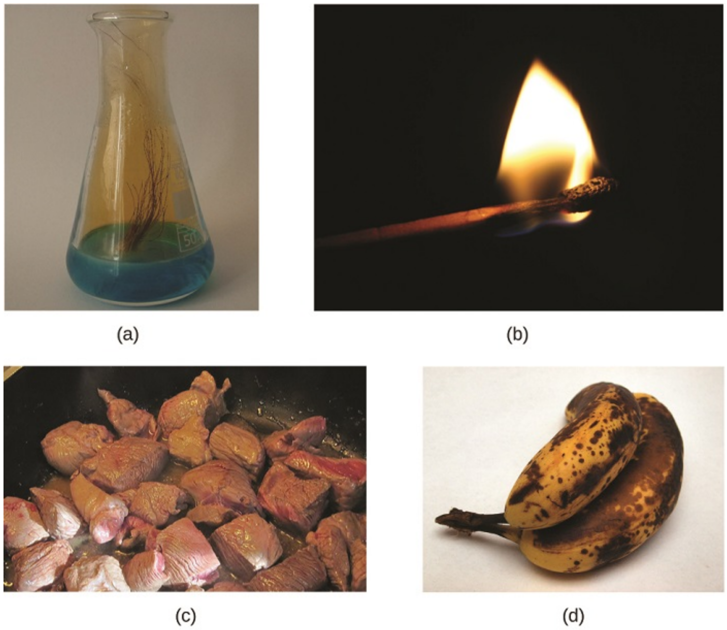

(a) (b)
(c) (d)

Figure $1.3.9$***:*** *(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)*

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

Summary

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

Contributors

- Modified by Joshua Halpern (Howard University)
- Tom Neils (Grand Rapids Community College)

1.4: A First Look at Energy

Skills to Develop

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 1.4.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

(a) Thermal energy

(b) Radiant energy

(c) Electrical energy

(d) Nuclear energy

(e) Chemical energy

Figure* 1.4.1*: *Forms of Energy. (a) Thermal energy results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) Radiant energy (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of electrical energy, which is due to the flow of electrically charged particles. (d) Nuclear energy is released when particles in the nucleus of the atom are rearranged. (e) Chemical energy results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.*

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy of an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 1.4.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

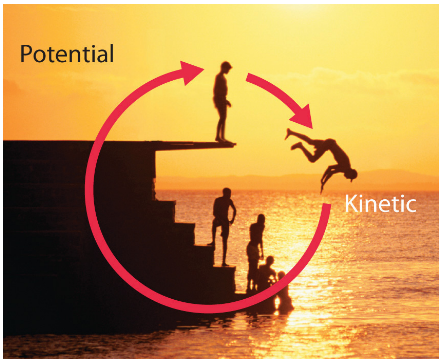


Figure* $1.4.2$*: *Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.*

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure $1.4.3$), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

work = force x distance

$$w = F\,d \tag{1.4.1}$$

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation $1.4.1$ as follows:

work= mass x acceleration x distance

$$w = m\,a\,d \tag{1.4.2}$$

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things:

1. the height of the second floor (the distance *d*);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

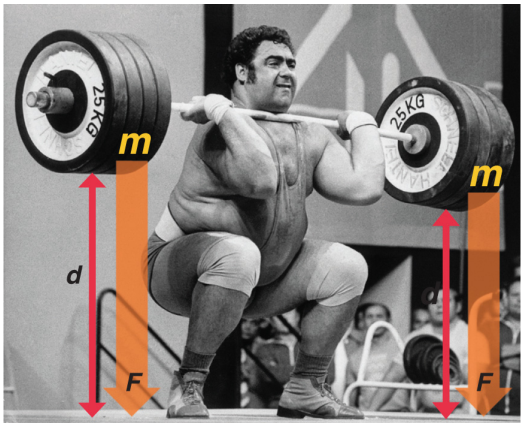


Figure 1.4.2: *An Example of Mechanical Work. One form of energy is mechanical work, the energy required to move an object of mass m a distance d when opposed by a force F, such as gravity.*

In contrast, heat (q) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

Energy is an *extensive* property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker.

A Mathematical Description of Kinetic Energy and Potential Energy

A Mathematical Description of Kinetic Energy and Potential Energy

$$KE = \frac{1}{2}mv^2 \tag{1.4.3}$$

The potential energy of an object is related to its position relative to another object or to a standard baseline (usually, the ground). As noted above, the energy required to move an object when opposed by a force (such as gravity), is:

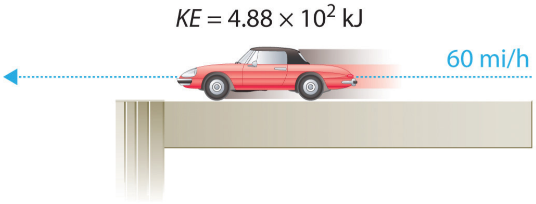
work = mass x acceleration x distance = force x distance

An Example

The kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) i

$$KE = \frac{1}{2}(1360kg)(26.8ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{1.4.4}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy. is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



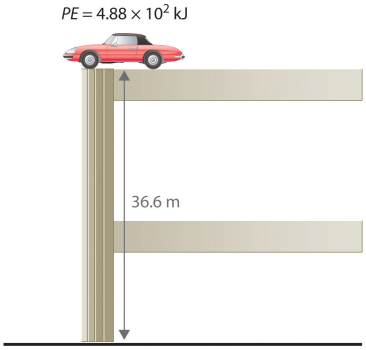
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is $w = Fd$. According to Equation 1.4.2, the force (F) exerted by gravity on any object is equal to its mass (m, in this case, 1360 kg) times the acceleration (a) due to gravity (g, 9.81 m/s^2 at Earth's surface). The distance (d) is the height (h) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$PE = F\,d = m\,a\,d = m\,g\,h \tag{1.4.5}$$

$$PE = (1360, Kg)\left(\frac{9.81\,m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{1.4.6}$$

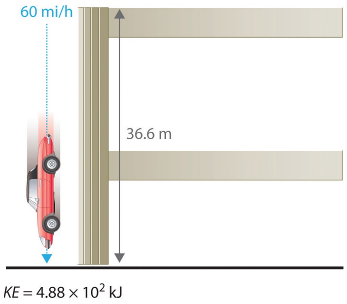
$$= 4.88 \times 10^5 J = 488\ kJ \tag{1.4.7}$$

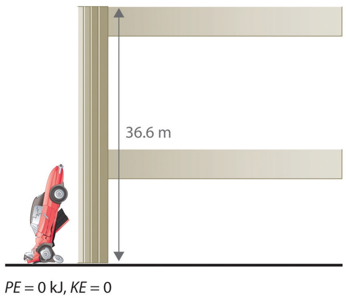
The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.





Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning "heat." Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ J \text{ exactly} \tag{1.4.8}$$

$$1\ J = 0.2390\ cal \tag{1.4.9}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

Example 1.4.1

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given: mass and velocity or height

Asked for: kinetic and potential energy

Strategy:

Use Equation 5.1.4 to calculate the kinetic energy and Equation 5.1.6 to calculate the potential energy, as appropriate.

Solution:

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$v=\left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right)=44.7\ m/s \tag{1.4.10}$$

The kinetic energy of the baseball is therefore

$$KE=\left(\frac{1}{2}\right)\times 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2=1.49\times 10^2\ \frac{kg\cdot m^2}{s^2}=1.49\times 10^2\ J \tag{1.4.11}$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$PE=149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)\left(247\ \cancel{ft}\right)\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right)=1.10\times 10^2\ \frac{kg\cdot m^2}{s^2}=1.10\times 10^2\ J \tag{1.4.12}$$

Exercise 1.4.1

a. In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer b

65 J

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work. *Thermochemistry* is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. The most common units of energy are the **joule (J)**, defined as 1 (kg·m^2)/s^2, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

Modified by Tom Neils (Grand Rapids Community College)

1.5: Making Measurements

Skills to Develop

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

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

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

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

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 1.5.1. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the International System of Units or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Table* 1.5.1*: *Base Units of the SI System*

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

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 1.5.2.

Table* 1.5.2*: *Common Unit Prefixes*

Prefix	**Symbol**	**Factor**	**Example**
femto	f	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)

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

SI Base Units

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

Length

The standard unit of length in both the SI and original metric systems is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 1.5.1); 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).

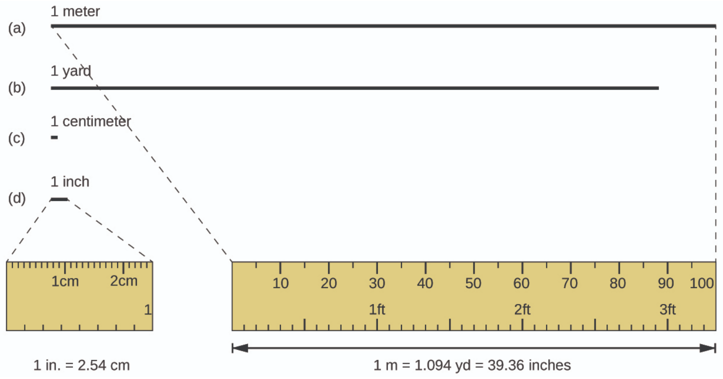


Figure 1.5.1: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

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

Figure 1.5.2: This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology).

Temperature

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

Time

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

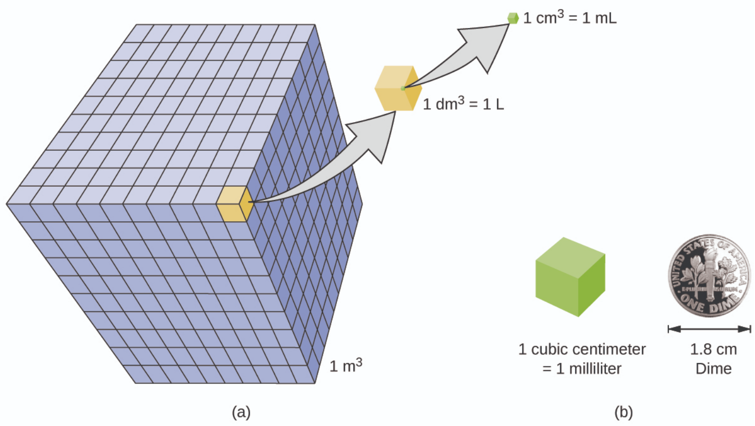
Derived SI Units

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

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 1.5.3). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

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



<

Figure 1.5.3: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

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

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table 1.5.3 shows the densities of some common substances.

Table 1.5.3: *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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.5.1}$$

Example 1.5.1

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.

$$\text{volume of lead cube} = 2.00\text{ cm} \times 2.00\text{ cm} \times 2.00\text{ cm} = 8.00\text{ cm}^3 onumber \tag{1.5.2}$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7\text{ g}}{8.00\text{ cm}^3} = \frac{11.3\text{ g}}{1.00\text{ cm}^3} = 11.3\text{ g/cm}^3 onumber \tag{1.5.3}$$

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

Exercise 1.5.1

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

Answer a

0.599 cm^3;

Answer b

8.91 g/cm^3

Example 1.5.2: Using Displacement of Water to Determine Density

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

Solution

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

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

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\text{ kg}}{1.25\text{ L}} = 4.00\text{ kg/L} \tag{1.5.4}$$

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

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\text{ kg}}{10.00\text{ L}} = 0.500\text{ kg/L} \tag{1.5.5}$$

Exercise 1.5.1

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

Answer

2.00 kg/L

Summary

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

Key Equations

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

Glossary

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

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

cubic meter (m^3)
SI unit of volume

density
ratio of mass to volume for a substance or object

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

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

length
measure of one dimension of an object

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

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

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

second (s)
SI unit of time

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

unit
standard of comparison for measurements

volume
amount of space occupied by an object

Contributors

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

1.6: Limits on Measurements

Skills to Develop

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

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

Significant Figures in Measurement

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

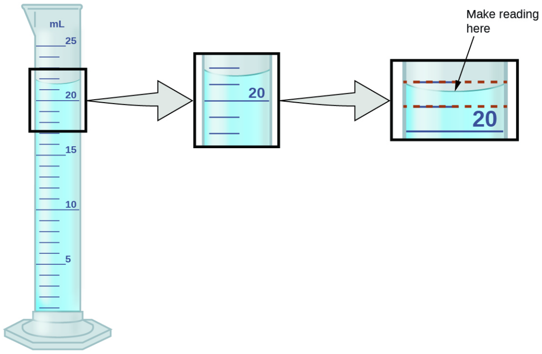
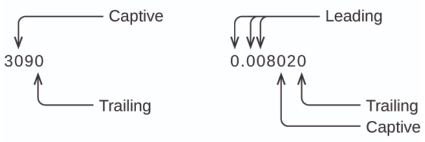


Figure 1.6.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in Figure 1.6.1. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

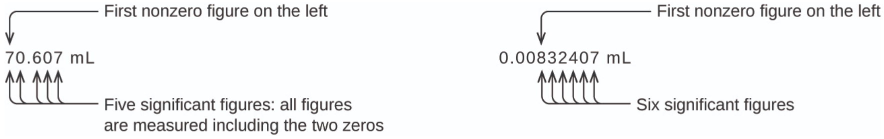
This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams.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

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



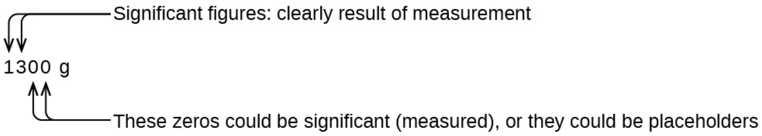
Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.

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



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

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



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

Significant Figures in Calculations

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

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we "round down" and leave the retained digit unchanged; if it is more than 5, we "round up" and increase the retained digit by 1; if the dropped digit *is* 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it's based on reliable statistics and is aimed at avoiding any bias when dropping the digit "5," since it is equally close to both possible values of the retained digit.)

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

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

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

Example 1.6.1: 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 1.6.1

Round the following to the indicated number of significant figures:

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

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

Example 1.6.2: Addition and Subtraction with Significant Figures Rule:

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

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

Solution

(a)

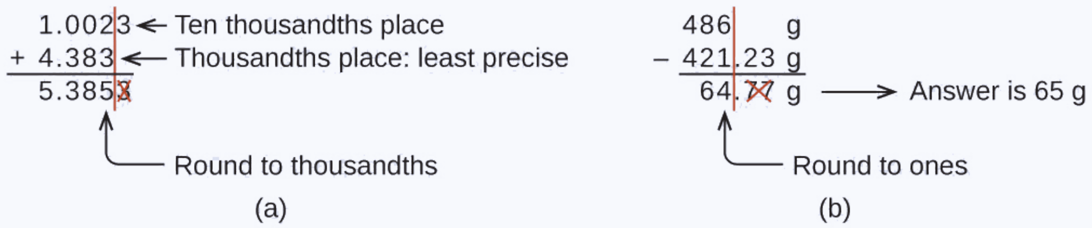
$$\begin{array}{r} 1.0023 \text{ g} \\ + \underline{4.383 \text{ g}} \\ 5.3853 \text{ g} \end{array}$$

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

(b)

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

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



(a) (b)

Exercise 1.6.2

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

Answer a

2.64 mL

Answer b

0.658 m

Example 1.6.3: Multiplication and Division with Significant Figures

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

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

Solution

(a)

$$0.6238 \text{ cm} \times 6.6 \text{ cm} = 4.11708 \text{ cm}^2 \rightarrow \text{result is } 4.1 \text{ cm}^2 \text{ (round to two significant figures)} \tag{1.6.1}$$

$$\text{four significant figures} \times \text{two significant figures} \rightarrow \text{two significant figures answer} \tag{1.6.2}$$

(b)

$$\frac{421.23 \text{ g}}{486 \text{ mL}} = 0.86728... \text{ g/mL} \rightarrow \text{result is } 0.867 \text{ g/mL (round to three significant figures)} \tag{1.6.3}$$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer} \tag{1.6.4}$$

Exercise 1.6.3

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

Answer a

0.747 cm^2

Answer b

0.9884 m/s

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

Example 1.6.4: Calculation with Significant Figures

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

Solution

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

Exercise 1.6.4: Determination of Density Using Water Displacement

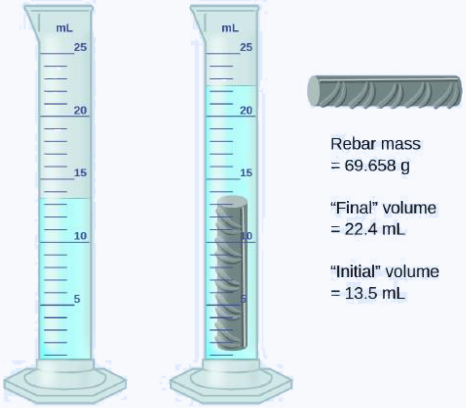
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 1.6.4

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



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

Solution

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

$$\text{volume} = 22.4 \text{ mL} - 13.5 \text{ mL} = 8.9 \text{ mL} = 8.9 \text{ cm}^3 onumber \tag{1.6.5}$$

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

The density is the mass-to-volume ratio:

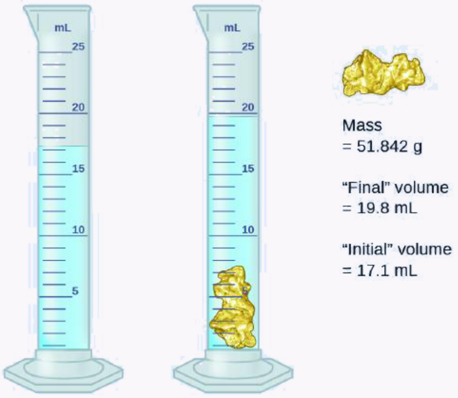
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658\text{ g}}{8.9\text{ cm}^3} = 7.8\text{ g/cm}^3 onumber \tag{1.6.6}$$

(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 1.6.4

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



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

Answer a

19 g/cm^3

Answer b

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

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.6.2).

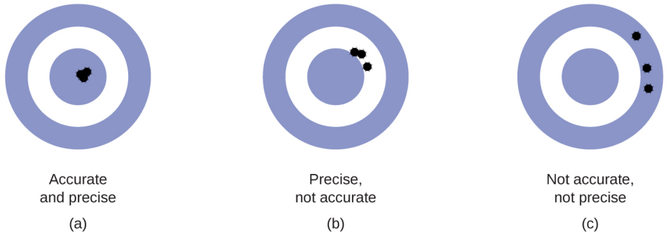


Figure 1.6.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither 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 1.6.2.

Table 1.6.2: *Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers*

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

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

Summary

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

Glossary

uncertainty

estimate of amount by which measurement differs from true value

significant figures

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

rounding

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

precision

how closely a measurement matches the same measurement when repeated

exact number

number derived by counting or by definition

accuracy

how closely a measurement aligns with a correct value

Contributors

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

1.7: Dimensional Analysis

Skills to Develop

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

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

$$\text{speed} = \frac{\text{distance}}{\text{time}} \tag{1.7.1}$$

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

$$\frac{100\text{ m}}{10\text{ s}} = \frac{10\text{ m}}{\text{s}} \tag{1.7.2}$$

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

$$\text{time} = \frac{\text{distance}}{\text{speed}} \tag{1.7.3}$$

The time can then be computed as:

$$25\text{ m} \times \frac{1\text{ s}}{10\text{ m}} = 2.5\text{ s} \tag{1.7.4}$$

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

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

Conversion Factors and Dimensional Analysis

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

$$\frac{2.54\text{ cm}}{1\text{ in.}}\ (2.54\text{ cm} = 1\text{ in.})\text{ or }2.54\,\frac{\text{cm}}{\text{in.}} \tag{1.7.5}$$

Several other commonly used conversion factors are given in Table $1.7.1$.

Table $\mathbf{1.7.1}$***:*** *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

Length	Volume	Mass
1 km = 0.62137 mi	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

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

$$34 \ \cancel{\text{in.}} \times \frac{2.54 \text{ cm}}{1 \ \cancel{\text{in.}}} = 86 \text{ cm} \tag{1.7.6}$$

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

$$\frac{\text{in.} \times \text{cm}}{\text{in.}}. \tag{1.7.7}$$

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

$$\frac{\text{in.}}{\text{in.}} = 1 \tag{1.7.8}$$

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

Example 1.7.1: Using a Unit Conversion Factor

The mass of a competition Frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 1.7.1).

Solution

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

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

We write the unit conversion factor in its two forms:

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

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

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

Exercise 1.7.1

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, such as multidimensional conversions. For example density is a two-dimensional property because it relates mass and volume. Thus, when you carry out a calculation involving density, you need to pay attention to both mass units and volume units. Fortunately, these units can be treated separately and independently, as shown in Example $1.7.2$, below. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 1.7.2: Computing Quantities from Measurement Results

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

Solution

Since $\text{density} = \frac{\text{mass}}{\text{volume}}$, 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 Table 1.7.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:

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

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

1. *Convert quarts to liters.*

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

2. *Convert liters to milliliters.*

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

Then,

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

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

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

Exercise 1.7.2

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

Answer

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

Example 1.7.3: Computing Quantities from Measurement Results

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

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

Solution

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

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

and then convert volume from liters to gallons:

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

Then,

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

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

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

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

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

Exercise 1.7.3

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

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

Answer a

51 mpg

Answer b

$62

Conversion of Temperature Units

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

To mark a scale on a thermometer, we need a set of reference values: Two of the most commonly used are the freezing and boiling temperatures of water at a specified atmospheric pressure. On the Celsius scale, 0 °C is defined as the freezing temperature of water and 100 °C as the boiling temperature of water. The space between the two temperatures is divided into 100 equal intervals, which we call degrees. On the Fahrenheit scale, the freezing point of water is defined as 32 °F and the boiling temperature as 212 °F. The space between these two points on a Fahrenheit thermometer is divided into 180 equal parts (degrees).

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

$$\text{length in feet} = \left(\frac{1\ \text{ft}}{12\ \text{in.}}\right) \times \text{length in inches} \tag{1.7.9}$$

where

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

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

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

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

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

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

The equation relating the temperature scales is then:

$$T_{{}^\circ\mathrm{F}} = \left(\frac{9\ {}^\circ\mathrm{F}}{5\ {}^\circ\mathrm{C}} \times T_{{}^\circ\mathrm{C}}\right) + 32\ {}^\circ\mathrm{C} \tag{1.7.10}$$

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

$$T_{{}^\circ\mathrm{F}} = \frac{9}{5} \times T_{{}^\circ\mathrm{C}} + 32 \tag{1.7.11}$$

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

$$T_{{}^\circ\mathrm{C}} = \frac{5}{9}(T_{{}^\circ\mathrm{F}} + 32) \tag{1.7.12}$$

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

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

$$T_{\mathrm{K}} = T_{{}^\circ\mathrm{C}} + 273.15 \tag{1.7.13}$$

$$T_{^\circ\mathrm{C}} = T_{\mathrm{K}} - 273.15 \tag{1.7.14}$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 1.7.1 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

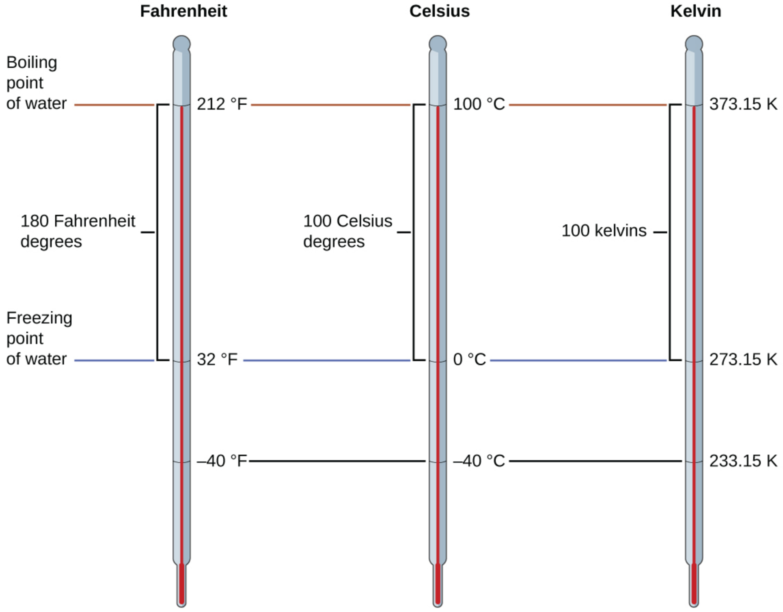


Figure 1.7.1: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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 1.7.4: 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

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

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

Exercise 1.7.4

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

Example 1.7.5: 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

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

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

Exercise 1.7.5

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

Summary

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

Key Equations

- $T_{^\circ\mathrm{C}} = \frac{5}{9} \times T_{^\circ\mathrm{F}} - 32$
- $T_{^\circ\mathrm{F}} = \frac{9}{5} \times T_{^\circ\mathrm{C}} + 32$
- $T_{\mathrm{K}} = {}^\circ\mathrm{C} + 273.15$
- $T_{^\circ\mathrm{C}} = \mathrm{K} - 273.15$

Glossary

dimensional analysis

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

Fahrenheit

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

unit conversion factor

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

Contributors

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

1.8: Matter, Measurement, and Problem Solving (Exercises)

Template:HideTOC

These are homework exercises to accompany the Textmap created for Chemistry: A Molecular Approach by Nivaldo Tro. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

Additional Questions

A1

Preform the following mathematical operations and give the answer with the correct number of significant figures:

a. $\dfrac{(9.008\times10^{4})(6.5227\times10^{7})}{6.53\times10^{-4}}$
b. $\sqrt{(7.1\times10^{2})+924}\,7.508\times10^{4}$
c. $\dfrac{(9.008\times10^{4})(6.5227\times10^{7})}{6.53\times10^{-4}}$

A2

Perform the following unit conversions. Express your answers in scientific notation with the appropriate number of significant figures.

a. Convert 78.01 inches into: feet, meters, centimeters, millimeters and kilometers.
b. Convert 14511 feet into miles, kilometers and meters.
c. Convert 15.42 meters into kilometers, centimeters, millimeters, micrometers, and nanometers.
d. Convert 98.6 °F into °C and K.
e. Convert 75 miles per hour into: km per hour and m s^{-1} .
f. Convert 23.15 m^{2} into ft2 , in2 , and cm^{2}

A3

In the movie Goldfinger, James Bond foils a plot to break into Fort Knox. 007 does some quick mental calculations to determine the feasibility of removing the gold. If the price of gold is $14.00 per troy ounce (31.1035 grams) at the time the movie was produced, what is the mass (in kg) of 1 million dollars of gold? What is the volume of 1 million dollars of gold in L. How much would this gold be worth today if the price of gold is $9068.77 per kg?

A4

The following experiment is performed with an unknown liquid. The liquid is added to a graduated cylinder with a mass of 54.6789 grams. After 20.00 mL of the liquid is added to the cylinder (at 298 K), the mass is 74.6215 grams. Is the liquid water? How do you know? If it is not water, what could it be?

A5

The experiment above is repeated with a second liquid, after 21.3 mL of this liquid (at 20 °C) is added the mass of the cylinder is 72.7364 grams. Is the second liquid ethanol? How do you know? If it is not ethanol, what could it be?

Answers

Exercise 1.8.1

A1

Answer

a) and c) (Sorry, I can't take out the repeat!) 9.00 x 10^{15} only 3 sig dig because of denominator

b) 9600 or 9.6 x 10^{3} only 2 sig dig because of 7.1 x 10^{2}

Exercise 1.8.2

A2

Answer

a) 6.501 ft; 1.981 m; 198.1 cm; 1981 mm; 1.981 x 10^{-3} km

b) 2.7483 miles; 4.4230 km; 4423.0 m

c) 0.01542 km; 1542 cm; 15,420 mm; 1.542 x 10^8 μm; 1.542 x 10^{11} pm

d) 37.0^{o}C; 310.2 K

e) 1.2 x 10^2 km/h; 34 m/s

f) 2.492 x 10^2 ft^2; 2.315 x 10^4 cm^2; 3.588 x 10^3 in^2

Exercise 1.8.3

A3

Answer

2.222 x 10^3kg; To get the volume you need the density of gold, which is 19.32 g/ml. The volume is 1.150 x 10^2 L; the value today is \$2.015 x 10^7

Exercise 1.8.4

A4

Answer

The density is found by first finding the mass of the liquid (74.6215-54.6789 = 19.9426 g), then dividing the mass by the volume (19.9426/20.00 = 0.9771 g/mL). That is the density of water at 25 ^{o}C. There are not any other common liquids with this density. You could create a mixture that has this density.

Exercise 1.8.5

A5

Answer

The density is found by first finding the mass of the liquid (72.7364-54.6789 = 18.0575 g), then dividing the mass by the volume (18.0575/21.3 = 0.848 g/mL). That is the not density of ethanol at 20 ^{o}C. The liquid could be mineral oil, which a mixture of many C_xH_y compounds.

CHAPTER OVERVIEW

2: Atomic Structure

2.1: Modern Atomic Theory and the Laws That Led to It

Skills to Develop

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 language used in chemistry is seen and heard in many disciplines, ranging from medicine to engineering to forensics to art. The language of chemistry includes its own vocabulary as well as its own form of shorthand. Chemical symbols are used to represent atoms and elements. Chemical formulas depict molecules as well as the composition of compounds. Chemical equations provide information about the quality and quantity of the changes associated with chemical reactions.

This chapter will lay the foundation for our study of the language of chemistry. The concepts of this foundation include the atomic theory, ion formation, the composition and mass of an atom, the variability of the composition of isotopes, nuclear stability, and atomic electronic structure. We will also discuss in greater detail one of the most powerful tools for organizing chemical knowledge: the periodic table.

Atomic Theory through the Nineteenth Century

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 $2.1.1$). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

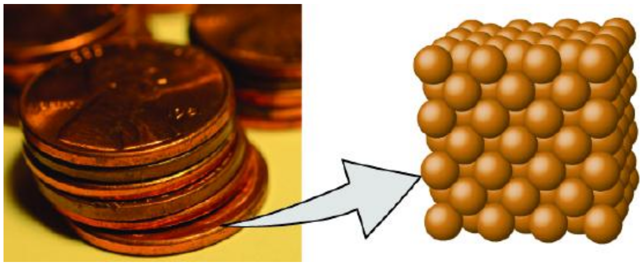


Figure $2.1.1$: *A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)*

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 $2.1.2$).

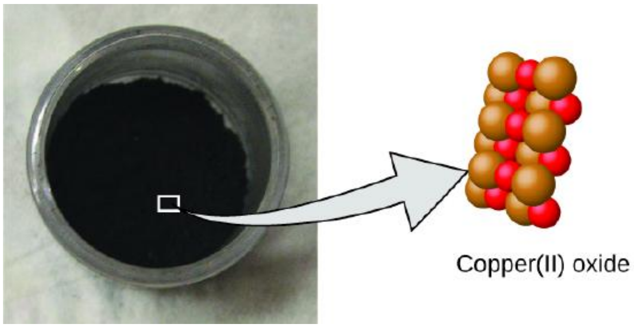


***Figure 2.1.2**: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)*

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 2.1.3).

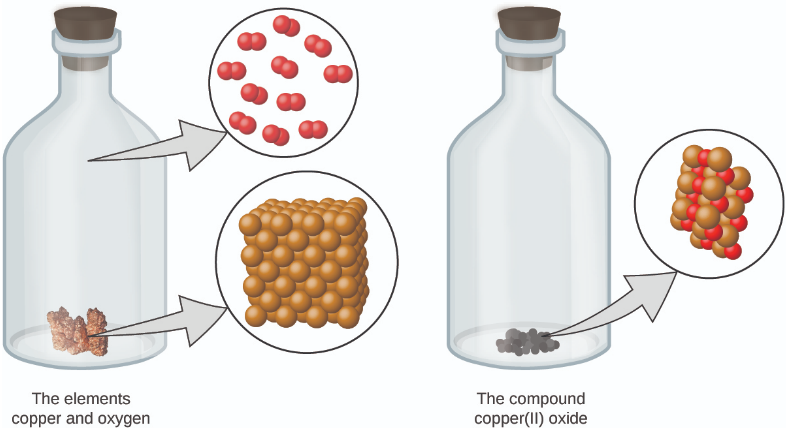
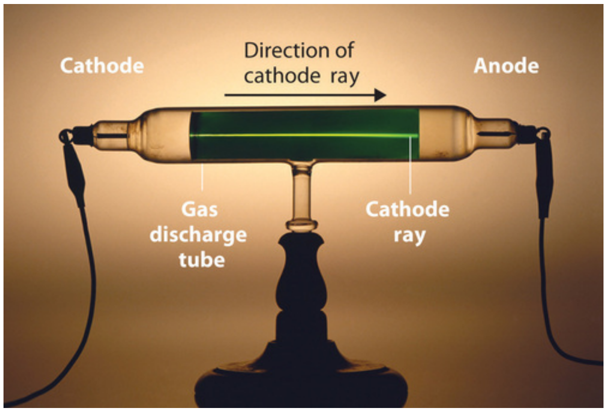


***Figure 2.1.3**: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of 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). We will see that Dalton's atomic theory was not entirely correct because Dalton was unaware of the existence of both isotopes and nuclear reactions.

Discovery of the Electron

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure 2.1.4). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the cathode, or negatively charged electrode; this form of energy was called a cathode ray.



Figure

Figure **2.1.4***: A Gas Discharge Tube Producing Cathode Rays. When a high voltage is applied to a gas contained at low pressure in a gas discharge tube, electricity flows through the gas, and energy is emitted in the form of light. Image used with Permission (CC BY-SA-NC).*

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 2.1.5) More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

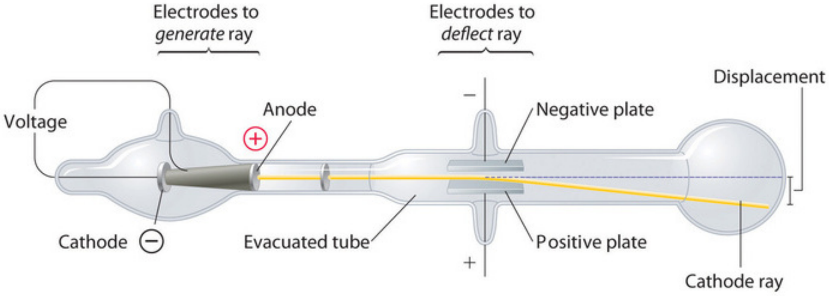


Figure **2.1.5***: Deflection of Cathode Rays by an Electric Field. As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged. Image used with Permission (CC BY-SA-NC).*

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

$$\frac{mass}{charge}\ x\ charge = mass$$

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

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

Radioactivity

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

***Figure* 2.1.6**: *Radium bromide illuminated by its own radioactive glow. This 1922 photo was taken in the dark in the Curie laboratory.*

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

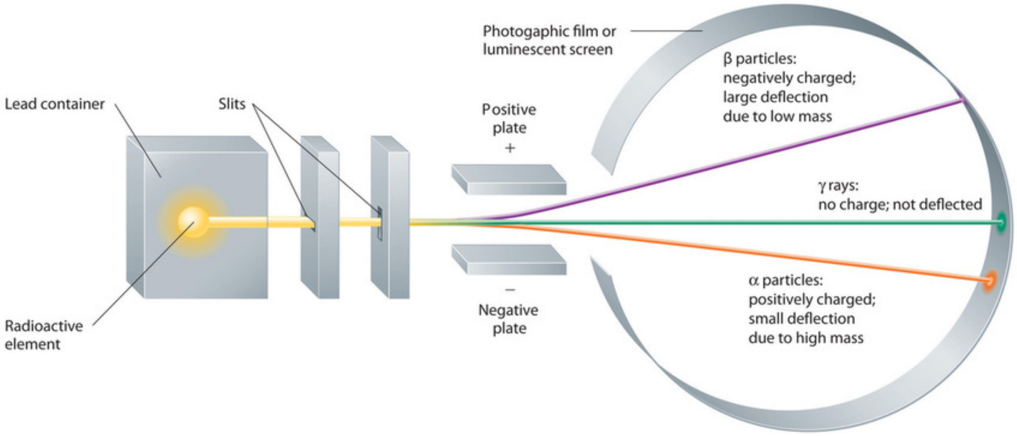


***Figure* $2.1.7$*: *Effect of an Electric Field on α Particles, β Particles, and γ Rays. A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.) Image used with Permission (CC BY-SA-NC).*

These three kinds of radiation—α particles, β particles, and γ rays—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As (Figure $2.1.7$) illustrates, α particles and β particles are deflected in opposite directions; α particles are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, γ rays have no charge, so they are not deflected by electric or magnetic fields. Figure $2.1.8$ hows that α particles have the least penetrating power and are stopped by a sheet of paper, whereas β particles can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, γ-rays can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

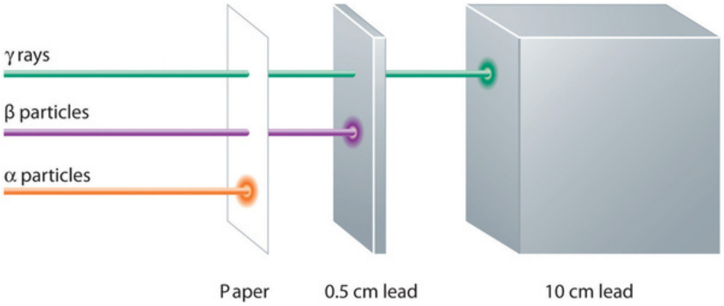


***Figure* $2.1.8$*: *Relative Penetrating Power of the Three Types of Radiation. A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them. Image used with Permission (CC BY-SA-NC).*

The Atomic Model

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure $2.1.9$)

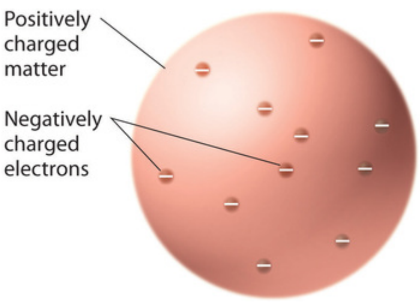
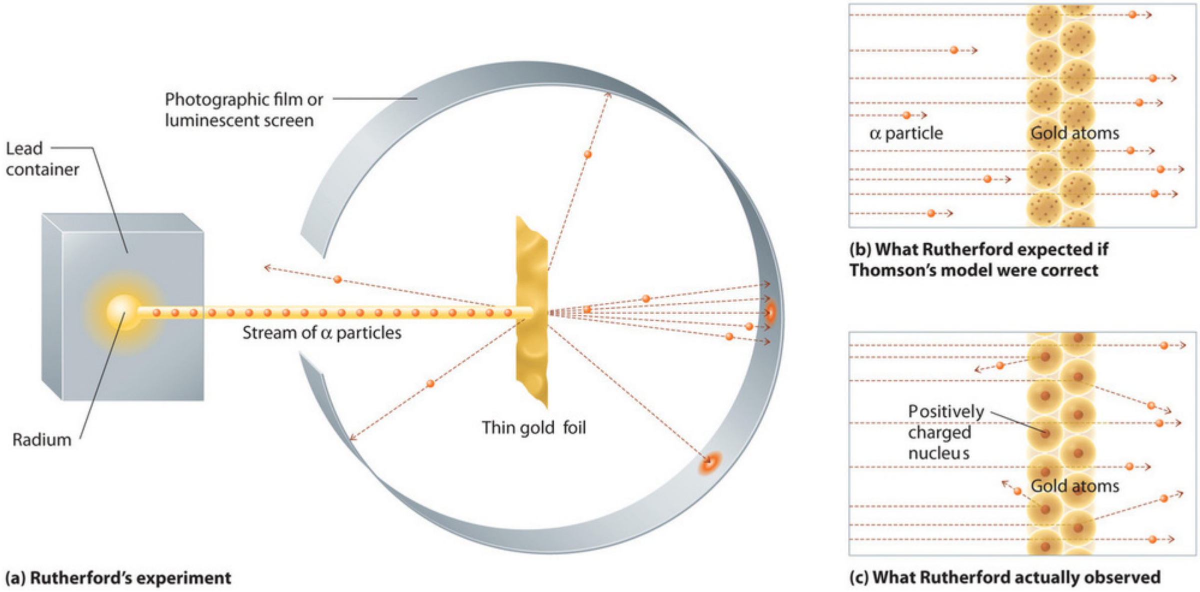


***Figure 2.1.9**: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge. Image used with Permission (CC BY-SA-NC).*

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (Figure 2.1.10a) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (Figure 2.1.10b). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (Figure 2.1.10c). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."



(a) Rutherford's experiment

(b) What Rutherford expected if Thomson's model were correct

(c) What Rutherford actually observed

***Figure 2.1.10**: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus. Image used with Permission (CC BY-SA-NC).*

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

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

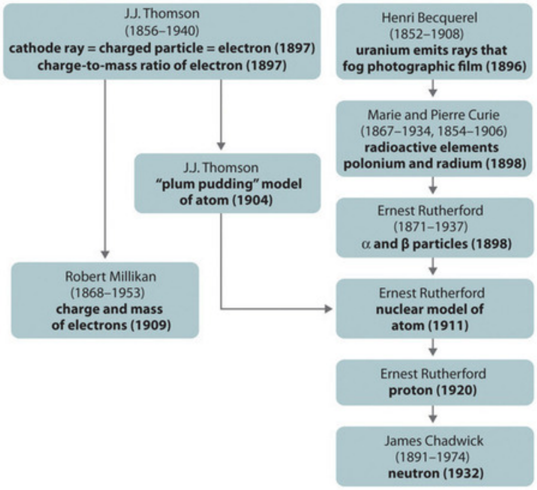


***Figure* $2.1.11$** *: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed. Image used with Permission (CC BY-SA-NC).*

The historical development of the different models of the atom's structure is summarized in (Figure $2.1.11$) Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name proton in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

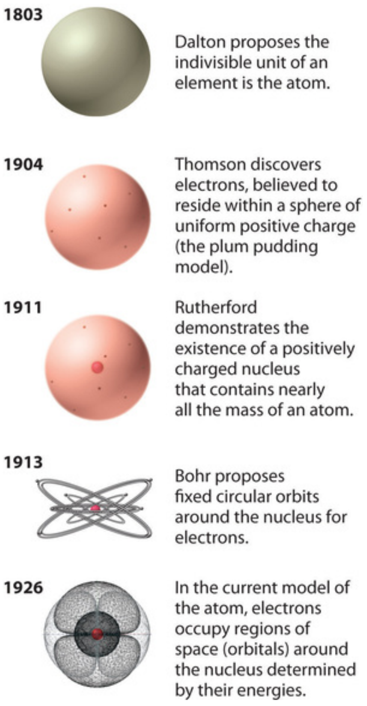


Figure $2.1.12$: *The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).*

Rutherford's model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics. Figure $2.1.12$ shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. During any chemical change, atoms are neither created nor destroyed. Atoms are the ultimate building blocks of all matter. The modern atomic theory establishes the concepts of atoms and how they compose matter.

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

Contributors

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

- Modified by Tom Neils (Grand Rapids Community College)

2.2 The Structure of the Atom

Skills to Develop

- 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 1).

***Figure 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 chapter.) Thus, one amu is exactly $1/12$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = -1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of $+1.602 \times 10^{-19}$ C. A neutron is a slightly heavier particle than a proton, with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of -1.602×10^{-19} C 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 1. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

***Table 1**: Properties of Subatomic Particles*

Name	Location	Charge (C)	Relative 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}

Name	Location	Charge (C)	Relative Charge	Mass (amu)	Mass (g)
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: the number of protons determines the identity of the atom**. For example, any atom that contains six protons is a carbon atom and has the atomic number 6, regardless of how many neutrons or electrons it may have.

A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its **mass number** (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

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

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

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

It is also true that:

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

As will be discussed in more detail later in this chapter, atoms (and molecules) 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**. A positively charged atom is called a **cation.** A cation is 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).

By convention, the charge of an ion is written as a superscript on the right side of the element symbol, with the magnitude of the charge written first, followed by the sign of the charge. Thus, the sodium ion with a +1 charge is written as Na^{1+} or simply Na^{+}. The sulfur ion with a -2 charge is written as S^{2-}.

Example 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).

Figure 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 an iodine anion.

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 1

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

Answer

78 protons; 117 neutrons; charge is +4

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 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).

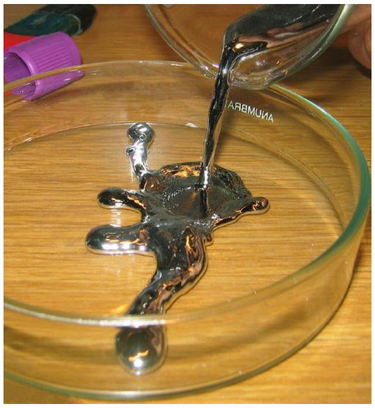


***Figure 3**: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. Image used with permission from Wikipedia (user: Materialscientist).*

The symbols for several common elements and their atoms are listed in Table 2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

***Table 2:** Some Common Elements and Their Symbols*

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)

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

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

Isotopes

Isotopes are atoms of the same element that have different numbers of neutrons. 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 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.

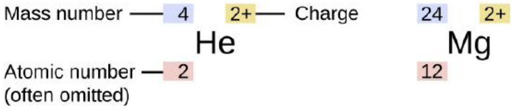


Figure 4: *The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.*

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 2. 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**: 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	$^{16}_{8}O$	8	8	8	15.9949	99.757
	$^{17}_{8}O$	8	8	9	16.9991	0.038
	$^{18}_{8}O$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}F$	9	9	10	18.9984	100

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
neon	$^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\text{Ne}$	10	10	12	21.9914	9.25

Atomic Mass

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

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

$$\text{weighted average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i \tag{1}$$

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

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

It is important to understand that no single boron atom weighs exactly 10.81 amu; 10.81 amu is the weighted average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

Example 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

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 3: Calculation of Percent Abundance

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

Solution

The weighted 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.

$$\text{weighted average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl}) \tag{2}$$

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

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

Substituting this into the average mass equation, we have:

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

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

Exercise 3

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

Answer

69.15% Cu-63 and 30.85% Cu-65

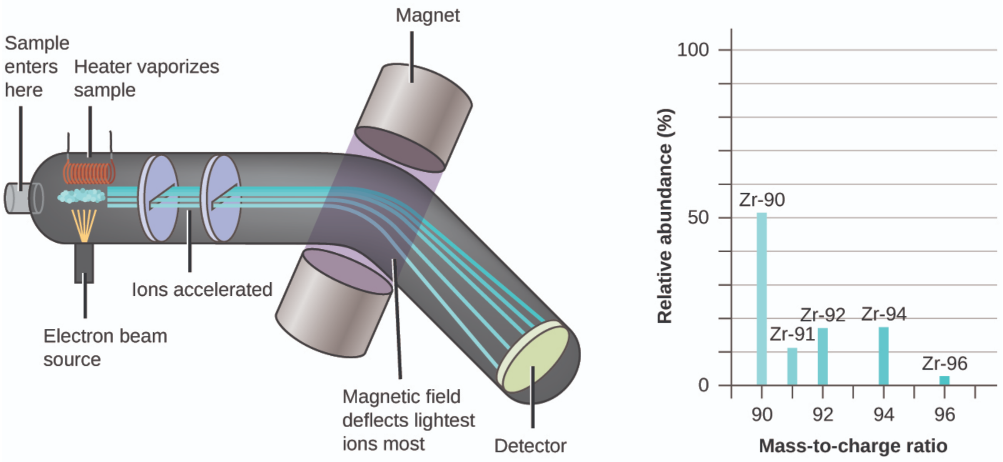


Figure 5: *Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.*

The occurrence and natural abundance 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 5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.

***Video 1**: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

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

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

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

Key Equations

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

Glossary

anion

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

atomic mass

average mass of atoms of an element, expressed in amu

atomic mass unit (amu)

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

atomic number (Z)

number of protons in the nucleus of an atom

cation

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

chemical symbol

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

Dalton (Da)

alternative unit equivalent to the atomic mass unit

fundamental unit of charge

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

ion

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

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

Contributors

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

- modified by Tom Neils (Grand Rapids Community College)

2.3 Molar Mass - Counting Atoms by Weighing Them

Skills to Develop

After reading this section you should be able to

- Define *Avogadro's number* and explain why it is important to know.
- Define the *mole*.
- Be able to calculate the number of moles in a given mass of an element, or the mass corresponding to a given number of moles.
- Define *atomic weight* and *molar mass*; explain how the latter differs from the former.
- Be able to find the number of atoms in a given mass of a substance.

The chemical changes we observe always involve *discrete numbers of atoms* that rearrange themselves into new configurations. These numbers are HUGE— far too large in magnitude for us to count or even visualize, but they are still *numbers*, and we need to have a way to deal with them. We also need a bridge between these numbers, which we are unable to measure directly, and the weights of substances, which we do measure and observe. The ***mole concept*** provides this bridge, and is central to all of quantitative chemistry.

Counting Atoms: Avogadro's Number

Owing to their tiny size, atoms and molecules cannot be counted by direct observation. But much as we do when "counting" beans in a jar, we can estimate the number of particles in a sample of an element or compound if we have some idea of the volume occupied by each particle and the volume of the container. Once this has been done, we know the number of formula units (to use the most general term for any combination of atoms we wish to define) in any arbitrary weight of the substance. The number will of course depend both on the formula of the substance and on the mass of the sample. However, if we consider a mass of substance that is the same as its atomic or molecular mass, expressed in grams, we have only one number to know: **Avogadro's number**, abbreviated as N_A.

Avogadro's number

Avogadro's number is known to nine significant digits:

$$N_A = 6.02214076 \times 10^{23}. \tag{1}$$

However, for most calculations you only need to know it to four significant figures:

$$N_A \approx 6.022 \times 10^{23}. \tag{2}$$

So 6.022×10^{23} of *what*? Well, of anything you like: apples, stars in the sky, burritos. However, the only *practical* use for N_A is for expressing the huge numbers of the tiny particles such as atoms or molecules that we deal with in chemistry. Avogadro's number is a *counting number*, just like a dozen (12 things), or a gross (144 things), or a ream (500 things). Students can think of 6.022×10^{23} as the "chemist's dozen".

Before getting into the use of Avogadro's number in problems, take a moment to convince yourself of the reasoning embodied in the following examples.

Example 1: Mass ratio from atomic weights

The atomic weights of oxygen and carbon are 16.0 and 12.0 atomic mass units (amu), respectively. How much heavier is the oxygen atom in relation to carbon?

Solution

Atomic weights represent the relative masses of different kinds of atoms. This means that the atom of oxygen has a mass that is

$$\frac{16\ \cancel{amu}}{12\ \cancel{amu}} = \frac{4}{3} \approx 1.33$$

as great as the mass of a carbon atom.

Example 2: Mass of a single atom

The absolute mass of a carbon atom is 12.0 atomic mass units (amu). How many grams will a single oxygen atom weigh?

Solution

The absolute mass of a carbon atom is 12.0 amu or

$$12\ \cancel{amu} \times \frac{1.6605 \times 10^{-24}\, g}{1\ \cancel{amu}} = 1.99 \times 10^{-23}\, g\, (\text{per carbon atom})$$

The mass of the oxygen atom will be 4/3 greater (from Example 1):

$$\left(\frac{4}{3}\right) 1.99 \times 10^{-23}\, g = 2.66 \times 10^{-23}\, g\, (\text{per oxygen atom})$$

Alternatively we can do the calculation directly like with carbon:

$$16\ \cancel{amu} \times \frac{1.6605 \times 10^{-24}\, g}{1\ \cancel{amu}} = 2.66 \times 10^{-23}\, g\, (\text{per oxygen atom})$$

Example 3: Relative masses from atomic weights

Suppose that we have N carbon atoms, where N is a number large enough to give us a pile of carbon atoms whose mass is 12.0 grams. How much would the same number, N, of oxygen atoms weigh?

Solution

We use the results from Example 1 again. The collection of N oxygen atoms would have a mass of

$$\frac{4}{3} \times 12\, g = 16.0\, g.$$

Exercise 1

What is the numerical value of N in Example 3?

Answer

Using the results of Examples 2 and 3.

$$N \times 1.99 \times 10^{-23}\, g\, (\text{per carbon atom}) = 12\, g$$

or

$$N = \frac{12\ \cancel{g}}{1.99 \times 10^{-23}\ \cancel{g}\ (\text{per carbon atom})} = 6.03 \times 10^{23} \text{atoms}$$

There are a lot of atoms in 12 g of carbon.

Things to understand about Avogadro's number

- It is a *number*, just as is "dozen", and thus is *dimensionless*.
- It is a *huge* number, far greater in magnitude than we can visualize
- Its practical use is limited to counting tiny things like atoms, molecules, "formula units", electrons, or photons.
- The value of N_A can be known only to the precision that the number of atoms in a measurable weight of a substance can be estimated. Because large numbers of atoms cannot be counted directly, a variety of ingenious indirect measurements have been made involving such things as Brownian motion and X-ray scattering.
- The current value was determined by measuring the distances between the atoms of silicon in an ultrapure crystal of this element that was shaped into a perfect sphere. (The measurement was made by X-ray scattering.) When combined with the measured mass of this sphere, it yields Avogadro's number. However, there are two problems with this:

- The silicon sphere is an artifact, rather than being something that occurs in nature, and thus may not be perfectly reproducible.
- The standard of mass, the kilogram, is not precisely known, and its value appears to be changing. For these reasons, there are proposals to revise the definitions of both N_A and the kilogram.

Moles and their Uses

The *mole* (abbreviated mol) is the the SI measure of *quantity of a "chemical entity"*, which can be an atom, molecule, formula unit, electron or photon. One mole of anything is just Avogadro's number of that something. Or, if you think like a lawyer, you might prefer the official SI definition:

Definition: The Mole

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.01200 kilogram of carbon 12

Avogadro's number (Equation 2) like any pure number, is dimensionless. However, it also defines the mole, so we can also express N_A as 6.022 × 10^{23} mol^{-1}; in this form, it is properly known as ***Avogadro's constant***. This construction emphasizes the role of Avogadro's number as a *conversion factor* between number of moles and number of "entities".

Example 4: number of moles in N particles

How many moles of nickel atoms are there in 80 nickel atoms?

Solution

$$80\ Ni\ atoms \times \frac{1\ mole\ Ni\ atoms}{6.022 \times 10^{23}\ Ni\ atoms} = 1.33 \times 10^{-22}\ mole\ Ni\ atoms$$

Is this answer reasonable? Yes, because 80 is an extremely small fraction of N_A.

Molar Mass

The mass of one mole of the fundamental units (atoms, molecules, or groups of atoms that correspond to the formula of a pure substance) is the ratio of its mass to 1/12 the mass of one mole of C-12 atoms, and being a ratio, is dimensionless. But at the same time, this *molar mass* (as many now prefer to call it) is also the observable mass of one mole (N_A) of the substance, so we frequently emphasize this by stating it explicitly as so many grams (or kilograms) per mole: g mol^{-1}.

> *It is important always to bear in mind that the mole is a number and not a mass. But each individual particle of a pure substance has a mass of its own, so a mole of any specific substance will always correspond to a certain mass, the molar mass, of that substance.*

Example 5: Manganese atoms

The molar mass of manganese (Mn) is 54.938 grams per mole

a. How many moles of manganese atoms are present in 20.0 g of manganese?
b. How many atoms of manganese are present in 20.0 g of manganese?
c. How many grams of manganese atoms are present in 3.47 x 10^{24} manganese atoms?

Solution

a.

$$20.0\ grams\ Mn\ atoms \times \frac{1\ mole\ Mn\ atoms}{54.938\ grams\ of\ Mn\ atoms} = 0.364\ moles\ of\ Mn\ atoms$$

b.

$$20.0\ grams\ Mn\ atoms \times \frac{1\ mole\ Mn\ atoms}{54.938\ grams\ of\ Mn\ atoms} \times \frac{6.022 \times 10^{23}\ Mn\ atoms}{1\ mole\ Mn\ atoms} = 2.19 \times 10^{23}\ Mn\ atoms$$

c.

$$3.47 \times 10^{24}\ Mn\ atoms \times \frac{1\ moleMn\ atoms}{6.022 \times 10^{23}\ Mn\ atoms} \frac{54.938\ grams\ of\ Mn\ atoms}{1\ moleMn\ atoms} = 317\ grams\ Mn\ atoms$$

Exercise 1

The molar mass of ruthenium (Ru) is 101.07 grams per mole

a. How many moles of ruthenium atoms are present in 200.0 g of manganese?
b. How many atoms of ruthenium are present in 200.0 g of manganese?
c. How many grams of ruthenium atoms are present in 3.47 x 10^{24} manganese atoms?

Answer

$$200.0\ grams\ Ru\ atoms \times \frac{1\ mole\ Ru\ atoms}{101.07\ grams\ of\ Ru\ atoms} = 1.979\ moles\ of\ Ru\ atoms$$

$$200.0\ grams\ Ru\ atoms \times \frac{1\ mole\ Ru\ atoms}{101.07\ grams\ of\ Ru\ atoms} \times \frac{6.022 \times 10^{23}\ Ru\ atoms}{1\ mole\ Ru\ atoms} = 1.192 \times 10^{24}\ Ru\ atoms$$

$$3.47 \times 10^{24}\ Ru\ atoms \times \frac{1\ mole Ru\ atoms}{6.022 \times 10^{23}\ Ru\ atoms} \frac{101.07\ grams\ of\ Ru\ atoms}{1\ mole Ru\ atoms} = 582.4\ grams\ Ru\ atoms$$

Contributors

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- modified by Tom Neils (Grand Rapids Community College)

2.4 Nuclear Reactions

Skills to Develop

- Write and balance nuclear equations
- Know the different kinds of radioactive decay.

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The sections on atoms, molecules, and ions introduced the basic idea of nuclear structure; that the nucleus of an atom is composed of protons and neutrons (with the exception of $^{1}_{1}\mathrm{H}$). Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation:

$$^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} \tag{1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called **nucleons**, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^{6} meters, 30,000 times larger).

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.

Nuclear Equations

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 subatomic particles are rearranged 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, $^{1}_{1}\mathrm{H}$, was one of the two products. Example 1 shows how we can identify a nuclide by balancing the nuclear reaction.

Example 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:

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

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:

$$25+4=\mathrm{A}+1 \tag{3}$$

so

$$\mathrm{A}=28 \tag{4}$$

Similarly, the charges must balance, so:

$$12+2=\mathrm{Z}+1 \tag{5}$$

so

$$\mathrm{Z}=13 \tag{6}$$

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

Exercise 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

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

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions**.** In a **nuclear decay reaction**, also called radioactive decay, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting daughter nuclei have a lower mass and are lower in energy (more stable) than the parent nucleus that decayed. In contrast, in a **nuclear transmutation reaction**, a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

> *Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.*

Nuclear Decay Reactions

Just as we use the number and type of atoms present to balance a chemical equation, we can use the number and type of nucleons present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, the total number of nucleons is conserved in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the ${}^{A}_{Z}\mathrm{X}$ notation for nuclides to include radioactive emissions. Table 1 lists the name and symbol for each type of emitted radiation. The most notable addition is the **positron**, a particle that has the same mass as an electron but a positive charge rather than a negative charge.

***Table 1**: Nuclear Decay Emissions and Their Symbols*

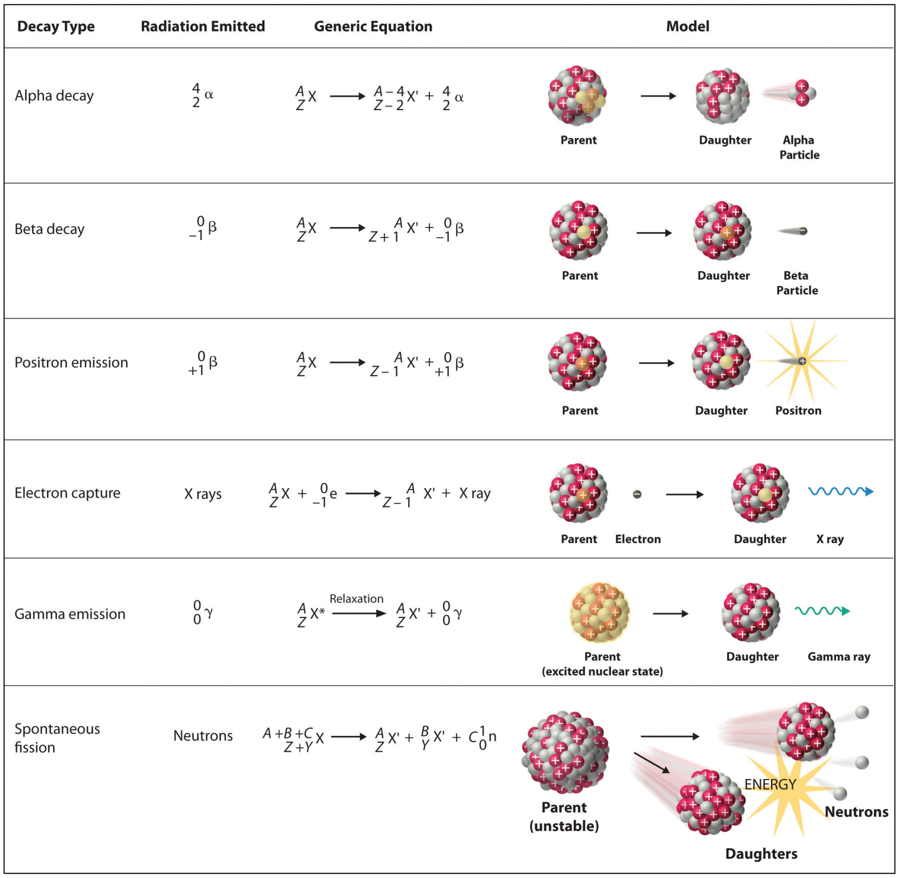
Identity	Symbol	Charge	Mass (amu)
helium nucleus	${}^{4}_{2}\alpha$	+2	4.001506
electron	${}^{0}_{-1}\beta$ or β^{-}	−1	0.000549

Identity	Symbol	Charge	Mass (amu)
photon	${}^{0}_{0}\gamma$	—	—
neutron	${}^{1}_{0}\mathrm{n}$	0	1.008665
proton	${}^{1}_{1}\mathrm{p}$	+1	1.007276
positron	${}^{0}_{+1}\beta$ or β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = -1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol ${}^{0}_{-1}\mathrm{e}$, which is usually simplified to e^{-}, represents a free electron or an electron associated with an atom, whereas the symbol ${}^{0}_{-1}\beta$, which is often simplified to β^{-}, denotes an electron that originates from within the nucleus, which is a β particle. Similarly, ${}^{4}_{2}\mathrm{He}^{2+}$ refers to the nucleus of a helium atom, and ${}^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 1. The most common are alpha and beta decay and gamma emission, but the others are essential to an understanding of nuclear decay reactions.



Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	${}^{4}_{2}\alpha$	${}^{A}_{Z}\mathrm{X} \longrightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^{4}_{2}\alpha$	Parent Daughter Alpha Particle
Beta decay	${}^{0}_{-1}\beta$	${}^{A}_{Z}\mathrm{X} \longrightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^{0}_{-1}\beta$	Parent Daughter Beta Particle
Positron emission	${}^{0}_{+1}\beta$	${}^{A}_{Z}\mathrm{X} \longrightarrow {}^{A}_{Z-1}\mathrm{X}' + {}^{0}_{+1}\beta$	Parent Daughter Positron
Electron capture	X rays	${}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{A}_{Z-1}\mathrm{X}' + \mathrm{X\ ray}$	Parent Electron Daughter X ray
Gamma emission	${}^{0}_{0}\gamma$	${}^{A}_{Z}\mathrm{X}^{*} \xrightarrow{\text{Relaxation}} {}^{A}_{Z}\mathrm{X}' + {}^{0}_{0}\gamma$	Parent (excited nuclear state) Daughter Gamma ray
Spontaneous fission	Neutrons	${}^{A+B+C}_{Z+Y}\mathrm{X} \longrightarrow {}^{A}_{Z}\mathrm{X}' + {}^{B}_{Y}\mathrm{X}' + C\,{}^{1}_{0}\mathrm{n}$	Parent (unstable) ENERGY Daughters Neutrons

Figure* 1: Common Modes of Nuclear Decay*

Alpha αDecay

Many nuclei with mass numbers greater than 200 undergo **alpha (α) decay**, which results in the emission of a helium-4 nucleus as an **alpha (α) particle**, ${}^{4}_{2}\alpha$. The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}\text{X}'} + \underset{\substack{\text{alpha}\\ \text{particle}}}{{}^{4}_{2}\alpha} \tag{7}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha \tag{8}$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

Note

Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

Beta β^- Decay

Nuclei that contain too many neutrons often undergo **beta (β) decay**, in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\substack{\text{unstable}\\ \text{neutron in}\\ \text{nucleus}}}{{}^{1}_{0}\text{n}} \rightarrow \underset{\substack{\text{proton}\\ \text{retained}\\ \text{by nucleus}}}{{}^{1}_{1}\text{p}} + \underset{\substack{\text{beta particle}\\ \text{emitted by}\\ \text{nucleus}}}{{}^{0}_{-1}\beta} \tag{9}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}\text{X}'} + \underset{\text{beta particle}}{{}^{0}_{-1}\beta} \tag{10}$$

Although beta decay does not change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta \tag{11}$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron β^+ Emission

Because a positron has the same mass as an electron but opposite charge, **positron emission** is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$${}^{1}_{1}\text{p}^{+} \rightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\beta^{+} \tag{12}$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}\text{X}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\text{X}'} + \underset{\text{positron}}{{}^{0}_{+1}\beta^{+}} \tag{13}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$$ {}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta^{+} \tag{14}$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or **electron capture (EC)**, in which an electron in an inner shell reacts with a proton to produce a neutron:

$$ {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{1}_{0}\mathrm{n} \tag{15}$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$ \underset{\text{parent}}{{}^{A}_{Z}\mathrm{X}} + \underset{\text{electron}}{{}^{0}_{-1}\mathrm{e}} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}\mathrm{X}'} + \text{x-ray} \tag{16}$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is lower by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$ {}^{55}_{26}\mathrm{Fe} \overset{\text{EC}}{\rightarrow} {}^{55}_{25}\mathrm{Mn} + \text{x-ray} \tag{17}$$

The atomic numbers of the parent and daughter nuclides differ in Equation 20.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$ {}^{55}_{26}\mathrm{Fe} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{55}_{25}\mathrm{Mn} + \text{x-ray} \tag{18}$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma γ Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. These high-energy photons are γ rays. **Gamma** (γ) **emission** can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$ {}^{238}_{92}\mathrm{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{{}^{234}_{90}\mathrm{Th}^{*}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma \tag{19}$$

If we disregard the decay event that created the excited nucleus, then

$$ {}^{234}_{88}\mathrm{Th}^{*} \rightarrow {}^{234}_{88}\mathrm{Th} + {}^{0}_{0}\gamma \tag{20}$$

or more generally,

$$ {}^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma \tag{21}$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of ${}^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$ {}^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4\,{}^{1}_{0}\text{n} \tag{22}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

Example 2

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of ${}^{35}_{16}\text{S}$
b. the decay of ${}^{201}_{80}\text{Hg}$ by electron capture
c. the decay of ${}^{30}_{15}\text{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of A and Z to identify any missing components needed to balance the equation.

Solution:

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}\text{X}$:

$$ {}^{35}_{16}\text{S} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{-1}\beta \tag{23}$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$ {}^{35}_{16}\text{S} \rightarrow {}^{35}_{17}\text{Cl} + {}^{0}_{-1}\beta \tag{24}$$

b.

A We know the identities of both reactants: ${}^{201}_{80}\text{Hg}$ and an inner electron, ${}^{0}_{-1}\text{e}$. The reaction is as follows:

$$ {}^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{A}_{Z}\text{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$ {}^{201}_{80}\text{Hg} + {}^{0}_{-1}\text{e} \rightarrow {}^{201}_{79}\text{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$ {}^{30}_{15}\text{P} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\text{P} \rightarrow \,^{30}_{14}\text{Si} + \,^{0}_{+1}\beta$$

Exercise 2

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\text{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\text{W}$

Answer a

$$^{11}_{6}\text{C} \rightarrow \,^{11}_{5}\text{B} + \,^{0}_{+1}\beta$$

Answer d

$$^{99}_{42}\text{Mo} \rightarrow \,^{99m}_{43}\text{Tc} + \,^{0}_{-1}\beta$$

Answer c

$$^{185}_{74}\text{W} \rightarrow \,^{181}_{72}\text{Hf} + \,^{4}_{2}\alpha + \,^{0}_{0}\gamma$$

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a **radioactive decay series**. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of “only” 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

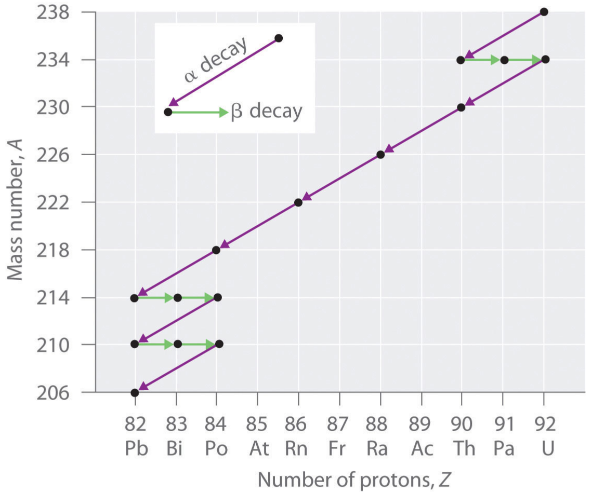


Figure 2 *A Radioactive Decay Series. Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.*

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$^{4}_{2}\alpha + {}^{14}_{7}\mathrm{N} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p}$$

Rutherford’s nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford’s at the time, named these neutral particles neutrons and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + {}^{9}_{4}\mathrm{Be} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n} \tag{25}$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}\mathrm{n} + {}^{14}_{7}\mathrm{N} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \tag{26}$$

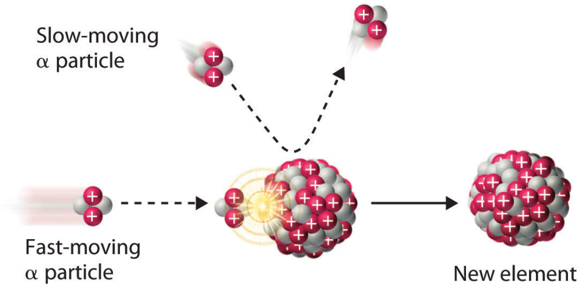


Figure 3 *A Nuclear Transmutation Reaction. Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.*

Example 4

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of Z and A of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution:

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (Z = 13) will be converted to phosphorus (Z = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target. In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, ${}^{30}_{15}\mathrm{P}$.

B The balanced nuclear equation for the reaction is as follows:

$${}^{27}_{13}\mathrm{Al} + {}^{4}_{2}\alpha \rightarrow {}^{30}_{15}\mathrm{P} + {}^{1}_{0}\mathrm{n} \tag{27}$$

Exercise 4

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei $\left({}^{2}_{1}\mathrm{H}\right)$ produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer

neutron, ${}^{1}_{0}\mathrm{n}$; ${}^{96}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{97}_{43}\mathrm{Tc} + {}^{1}_{0}\mathrm{n}$:

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as ${}^{235}_{92}\mathrm{U}$ and ${}^{239}_{94}\mathrm{Pu}$ undergo induced nuclear fission when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 4:

$${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{236}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} \tag{28}$$

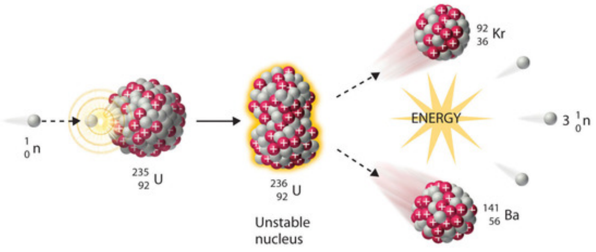


Figure 4 Neutron-Induced Nuclear Fission. *Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.*

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a **fissile isotope**.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 5, a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

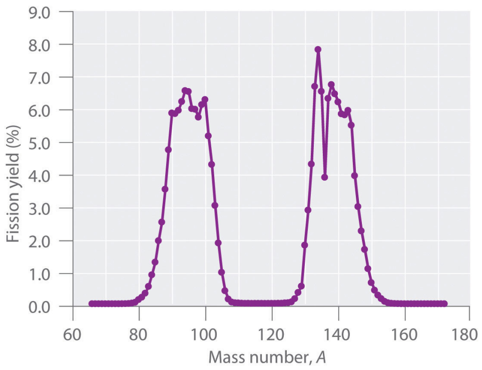


Figure 5 Mass Distribution of Nuclear Fission Products of ^{235}U. *Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for*^{235}*U. Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).*

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with $Z > 92$, the **transuranium elements**, are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 20.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{239}_{92}\text{U} \rightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\beta$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\text{Np} \rightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\beta$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability."

Table 2: *Some Reactions Used to Synthesize Transuranium Elements*

$^{239}_{94}\text{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
$^{239}_{94}\text{Pu} + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}\text{Am} + {}^{1}_{1}\text{p} + {}^{1}_{0}\text{n}$
$^{242}_{96}\text{Cm} + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}\text{Bk} + {}^{1}_{1}\text{p} + 2{}^{1}_{0}\text{n}$
$^{253}_{99}\text{Es} + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
$^{238}_{92}\text{U} + {}^{12}_{6}\text{C} \rightarrow {}^{246}_{98}\text{Cf} + 4{}^{1}_{0}\text{n}$
$^{252}_{98}\text{Cf} + {}^{10}_{5}\text{B} \rightarrow {}^{256}_{103}\text{Lr} + 6{}^{1}_{0}\text{n}$

A device called a particle accelerator is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

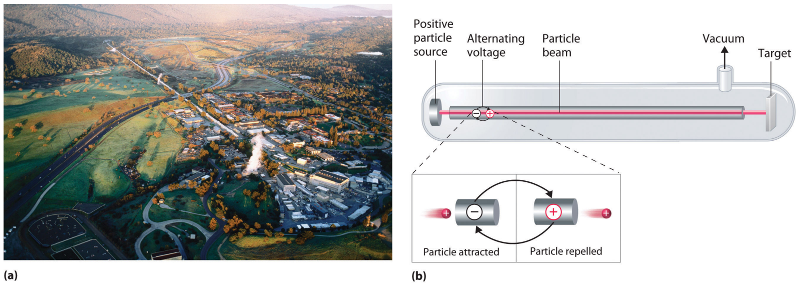


***Figure* 6**: *A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.*

To achieve the same outcome in less space, a particle accelerator called a cyclotron forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a synchrotron, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter. Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.

Summary and Key Takeaway

- Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

In **nuclear decay reactions (or radioactive decay)**, the parent nucleus is converted to a more stable daughter nucleus. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. *Alpha decay* results in the emission of an α particle, ${}^4_2\alpha$, and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a nuclear excited state undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in particle accelerators such as linear accelerators, cyclotrons, and synchrotrons.

Key Equations

alpha decay

$${}^A_Z\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{X}' + {}^4_2\alpha$$

beta decay

$${}^A_Z\mathrm{X} \rightarrow {}^{A}_{Z+1}\mathrm{X}' + {}^0_{-1}\beta$$

positron emission

$$ {}_{Z}^{A}\mathrm{X} \rightarrow {}_{Z-1}^{\ \ A}\mathrm{X}' + {}_{+1}^{\ \ 0}\beta $$

electron capture

$$ {}_{Z}^{A}\mathrm{X} + {}_{-1}^{\ \ 0}\mathrm{e} \rightarrow {}_{Z-1}^{\ \ A}\mathrm{X}' + \text{x-ray} $$

gamma emission

$$ {}_{Z}^{A}\mathrm{X}^{*} \rightarrow {}_{Z}^{A}\mathrm{X} + {}_{0}^{0}\gamma $$

modified by Tom Neils (Grand Rapids Community College)

2.5 The Belt of Stability - Predicting the Type of Radioactivity

Skills to Develop

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or decay, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that are the main focus of all the other chapters, and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

Each element can be represented by the notation ${}^{A}_{Z}\mathrm{X}$, where A, the mass number, is the sum of the number of protons and the number of neutrons, and Z, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

${}^{A}_{Z}\mathrm{X}$	${}^{16}_{8}\mathrm{O}$	${}^{17}_{8}\mathrm{O}$	${}^{18}_{8}\mathrm{O}$
${}^{A}\mathrm{X}$	${}^{16}\mathrm{O}$	${}^{17}\mathrm{O}$	${}^{18}\mathrm{O}$
element-A:	oxygen-16	oxygen-17	oxygen-18

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17. Any nucleus that is unstable and decays spontaneously is said to be **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the **strong nuclear force**, an extremely powerful but very short-range attractive force between nucleons (Figure 1). All stable nuclei except the hydrogen-1 nucleus (${}^{1}\mathrm{H}$) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

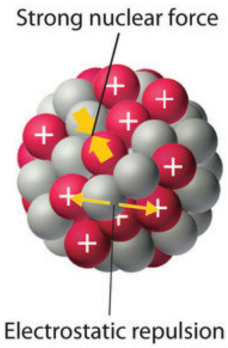


Figure* 1: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.*

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 2. The stable isotopes form a "peninsula of stability" in a "sea of instability." Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $^4_2$He, $^{10}_5$B, and $^{40}_{20}$Ca). All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with Z > 83 are unstable and radioactive.

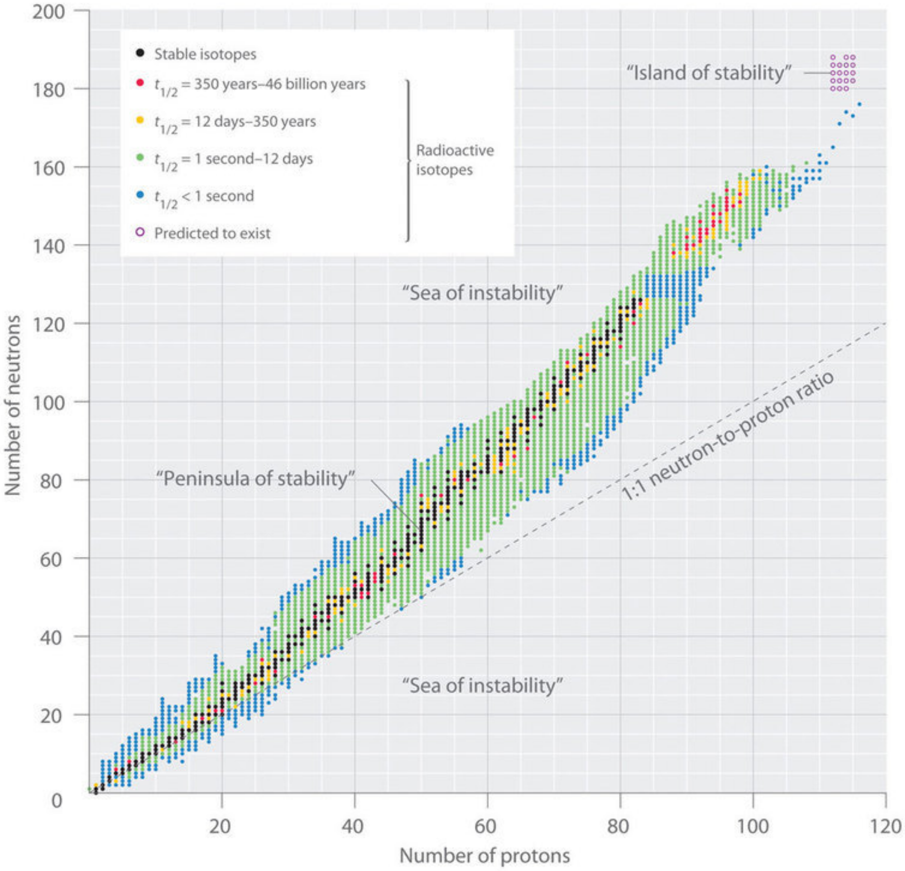


Figure* 2: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized. Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.*

As shown in Figure 3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be "doubly magic" and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}\text{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\text{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

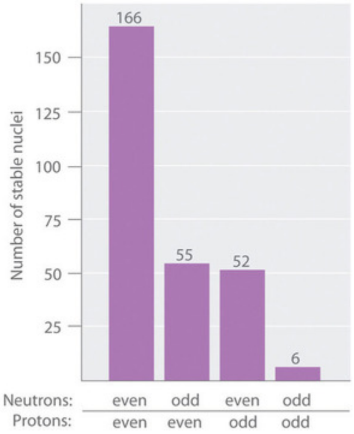


Figure 3: *The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.*

> *Most stable nuclei contain **even** numbers of both neutrons and protons*

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 2, the “peninsula” of stable isotopes is surrounded by a “reef” of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

Superheavy Elements

In addition to the “peninsula of stability” there is a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the **superheavy elements**, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with Z = 114 and Z = 116 have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an “eternity” by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with A = 292 that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with Z = 122. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

modified by Tom Neils (Grand Rapids Community College)

2.6 Half-lives and the Rate of Radioactive Decay

Skills to Develop

- To know how to use half-lives to describe the rates of first-order reactions

Radioactive Decay Rates

Radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. Because there are so many unstable nuclei that decay, we need a method to describe and compare the rates at which these nuclei decay. One approach to describing reaction rates is based on the time required for the number of unstable nuclei to decrease to one-half the initial value. This period of time is called the **half-life** of the process, written as $t_{1/2}$. Thus the half-life of a nuclear decay process is the time required for the number of unstable nuclei to decrease from $[A]_0$ to $1/2[A]_0$.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after n half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

> *For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].*

For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.6, along with some of their applications.

***Table* 2**: *Half-Lives and Applications of Some Radioactive Isotopes*

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Radioactive Isotope	Half-Life	Typical Uses
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth’s crust
americium-241	432.2 yr	smoke detectors
*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.		

Note

Radioactive decay is a first-order process.

Example 1

If you have a 120 gram sample of a radioactive element, how many grams of that element will be left after 3 half-lives have passed?

Solution

Given: mass of radioactive sample of an element, number of half-lives

Asked to Solve For: mass of radioactive element after so many half-lives

Solve:

All radioactive samples lose half of their mass after each half-life. Thus, one solution is to calculate the mass after each half-life. (This method only works if you are asked to solve for a whole number of half-lives). Let the passing of time equal to one half-life be represented by and arrow, →. Then the solution is:

$$120\text{ g} \rightarrow 60\text{ g} \rightarrow 30\text{ g} \rightarrow 15\text{ g}$$

If you want to solve for any number of half-lives, including fractional half-lives, then you use the equation: amount remaining = $\left(\frac{1}{2}\right)^n (amount\ at\ start)$, where n= number of half-lives. Then the solution is:

$$\text{amount remaining} = \left(\frac{1}{2}\right)^3 (120g) = 15g$$

Exercise 1

If you have a 300. gram sample of a radioactive element, how many grams of that element will be left after 4.30 half-lives have passed?

Answer

$$\text{amount left} = \left(\frac{1}{2}\right)^{4.30} (300.g) = 15.2g$$

Exercise 2

A certain radioactive nuclide has a half-life of 5.25 days. If you start with 100. grams of this nuclide, how many grams of the nuclide will be left after 20.0 days?

Answer

$$20.0\ days \times \frac{1\ half-life}{5.25\ days} = 3.81\ half-lives$$

$$\text{amount left} = \left(\frac{1}{2}\right)^{3.81} (100.g) = 7.13g$$

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth’s atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^- \tag{1}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon. Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11.Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The rate of decay, or activity, of a sample of a radioactive substance is the rate of decrease in the number of radioactive nuclei per unit time. The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. Radioactive decay reactions are first-order reactions.

Modified by Tom Neils (Grand Rapids Community College)

2.7 Mass Defect - The Source of Nuclear Energy

Skills to Develop

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) is expressed in the following equation:

$$E = mc^2 \tag{1}$$

where

- c is the speed of light ($2.998 \times 10^8\ m/s$), and
- E and m are expressed in units of joules and kilograms, respectively.

Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 1, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? The solution to this apparent contradiction is that chemical reactions are indeed accompanied by changes in mass, but these changes are simply too small to be detected. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -393.5\ \mathrm{kJ/mol} \tag{2}$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. When a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, ΔE ≈ ΔH. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)c^2 \tag{3}$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2} \tag{4}$$

Because 1 J = 1 $(\mathrm{kg{\bullet}m^2})/\mathrm{s^2}$, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ \mathrm{kJ/mol}}{(2.998 \times 10^8\ \mathrm{m/s})^2} = \frac{-3.935 \times 10^5 (\mathrm{kg \cdot m^2})/(\mathrm{s^2 \cdot mol})}{(2.998 \times 10^8\ \mathrm{m/s})^2} = -4.38 \times 10^{-12}\ \mathrm{kg/mol} \tag{5}$$

This is a mass change of about 3.6×10^{-10} g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + {}^{0}_{-1}\beta \tag{6}$$

We can use the experimentally measured masses of subatomic particles and common isotopes given in Table 20.1 to calculate the change in mass directly. The reaction involves the conversion of a neutral ^{14}C atom to a positively charged ^{14}N ion (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ^{14}N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\begin{aligned} \Delta m &= \text{mass}_{\text{products}} - \text{mass}_{\text{reactants}} \qquad (7) \\ &= 14.003074 \text{ amu} - 14.003242 \text{ amu} = -0.000168 \text{ amu} \qquad (8) \end{aligned}$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ^{14}C is −0.000168 g = -1.68×10^{-4} g = -1.68×10^{-7} kg. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

$$\begin{aligned} \Delta E &= (\Delta m)c^2 = (-1.68 \times 10^{-7} \text{ kg})(2.998 \times 10^8 \text{ m/s})^2 \qquad (9) \\ &= -1.51 \times 10^{10} (\text{kg} \cdot \text{m}^2)/\text{s}^2 = -1.51 \times 10^{10} \text{ J} = -1.51 \times 10^7 \text{ kJ} \qquad (10) \end{aligned}$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$(-1.68 \times 10^{-4} \text{ amu}) \left(\frac{931 \text{ MeV}}{\text{amu}} \right) = -0.156 \text{ MeV} = -156 \text{ keV}$$

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^1H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^2H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$\begin{aligned} m_{^2\text{H}} &= m_{\text{neutron}} + m_{\text{proton}} + m_{\text{electron}} \qquad (11) \\ &= 1.008665 \text{ amu} + 1.007276 \text{ amu} + 0.000549 \text{ amu} = 2.016490 \text{ amu} \qquad (12) \end{aligned}$$

The difference between the sum of the masses of the components and the measured atomic mass is called the **mass defect** of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 4, this release of energy must be accompanied by a decrease in the mass of the nucleus.

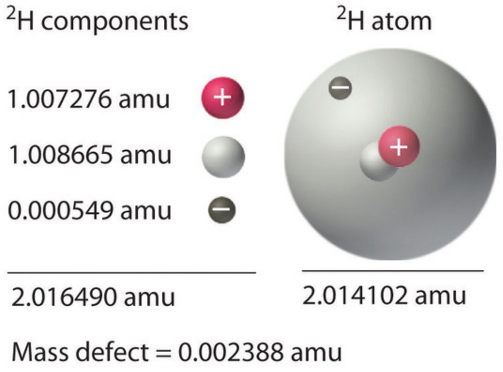


Figure 1: *Nuclear Binding Energy in Deuterium. The mass of a ^2H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the*

mass defect, the greater the nuclear binding energy and the more stable the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the **nuclear binding energy** (Figure 1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

> *Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.*

Not all nuclei are equally stable. Chemists describe the relative stability of different nuclei by comparing the binding energy per nucleon, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 2, the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

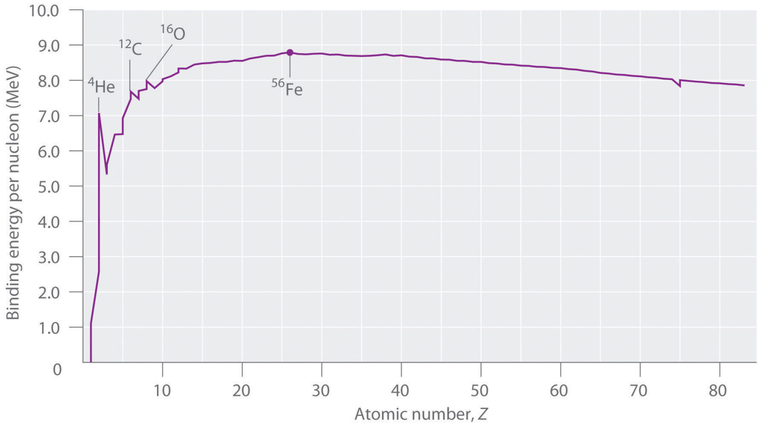


***Figure 2**: The Curve of Nuclear Binding Energy. This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.*

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in Figure 2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

> *Heavier nuclei spontaneously undergo nuclear reactions that decrease their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that increase their atomic number.*

Summary

Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation. Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of ^{1}H, the experimentally determined mass of an atom is always less than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the mass defect of the nucleus. The energy corresponding to the mass defect is the nuclear binding energy, the amount of energy released when a nucleus forms from its component particles. In nuclear fission, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The critical mass is the minimum mass required to support a self-sustaining nuclear chain reaction. Nuclear fusion is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

2.8 Nuclear Energy - Fission and Fusion

Skills to Develop

- Explain nuclear fission
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 1.

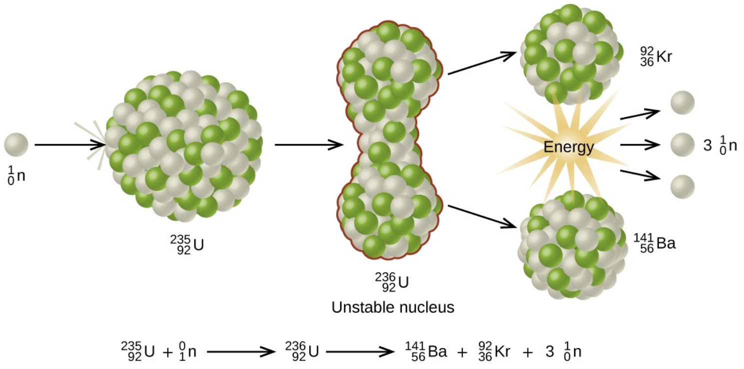


Figure 1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

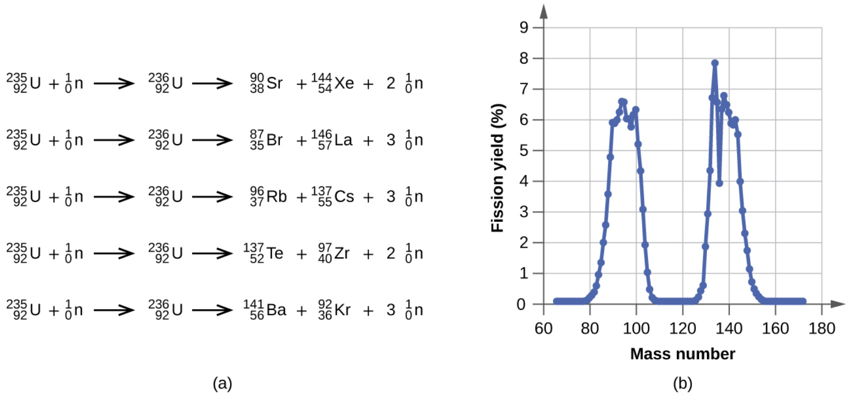


Figure 2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

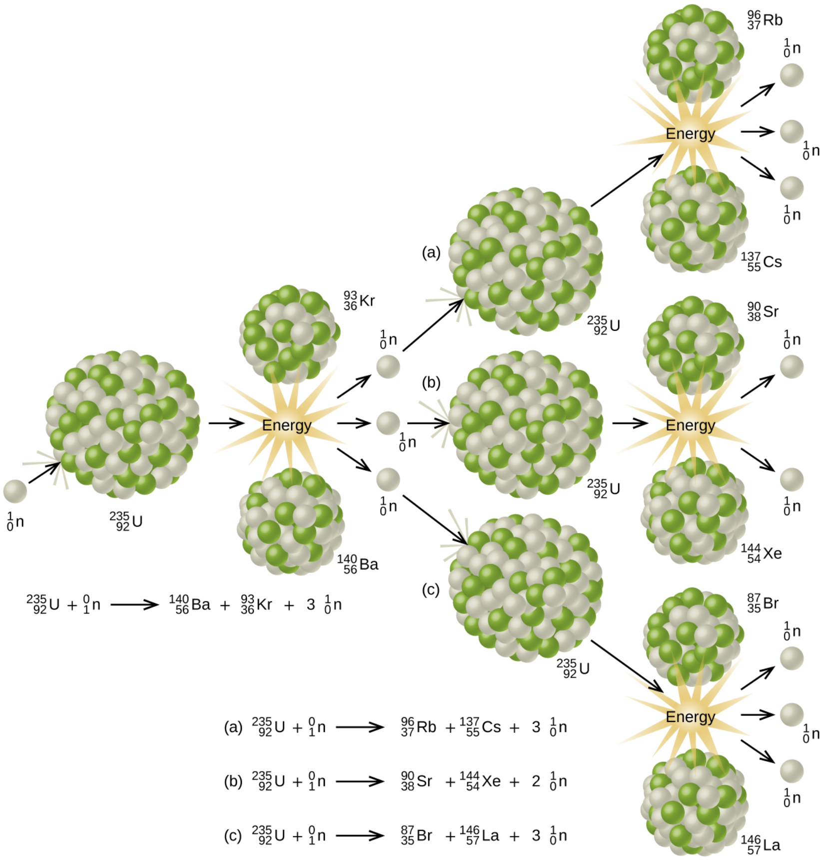


Figure 3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 4).

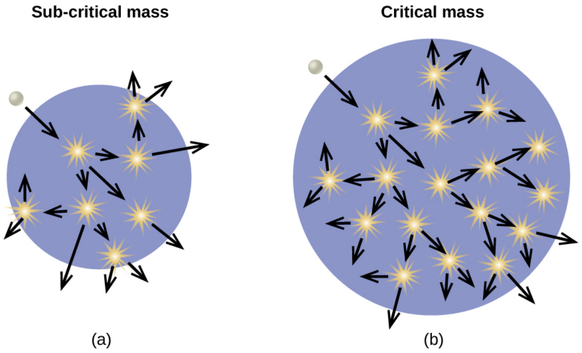


Figure 4: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 5) contains several pounds of fissionable material, $^{235}_{92}\text{U}$ or $^{239}_{94}\text{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

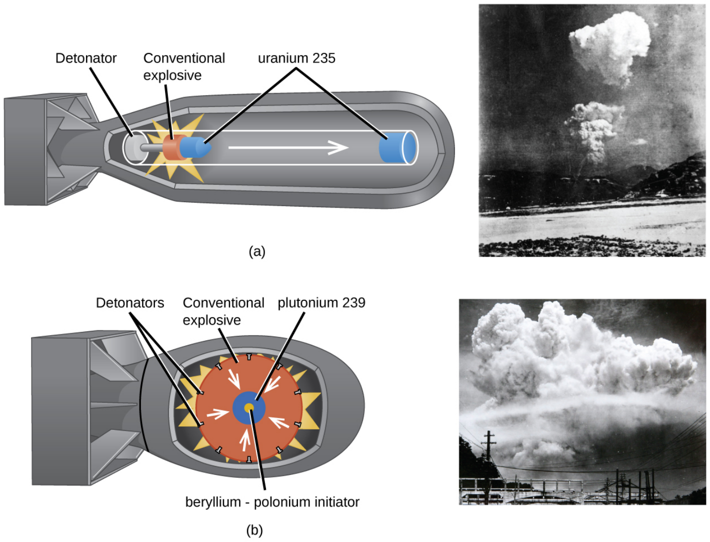


Figure* 5*: *(a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.*

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure 6). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

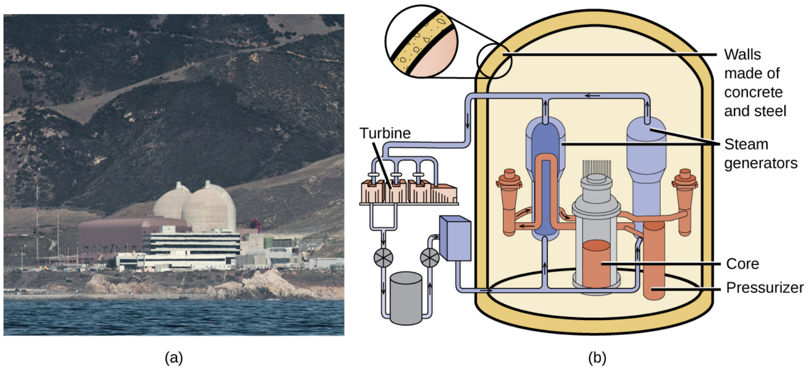


Figure 6: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3%

nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham's law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure 4). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water $\left({}^{2}_{1}\mathrm{H}_2\mathrm{O}\right)$ or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$ {}^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} \tag{1}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

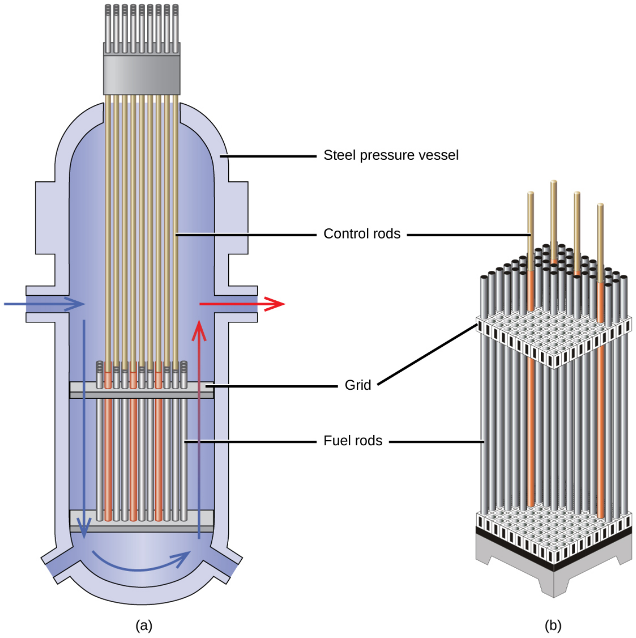


Figure 7: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossar...en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

***Video 1**: Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.*

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

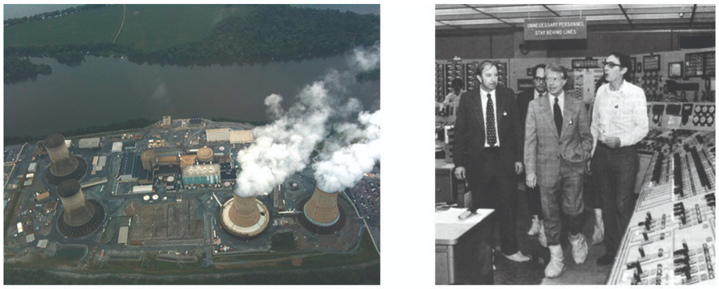
The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g) \tag{2}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 8).



(a) (b)

Figure 8: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 10).

(a) (b)

***Figure 9**: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)*

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Fusion

Skills to Develop

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{n} \tag{3}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}H$ and a triton, ${}^{3}_{1}H$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{4}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of ${}^{4}_{2}\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

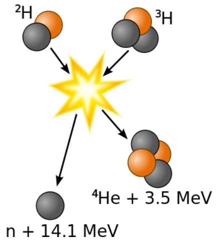


Figure 1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 2).

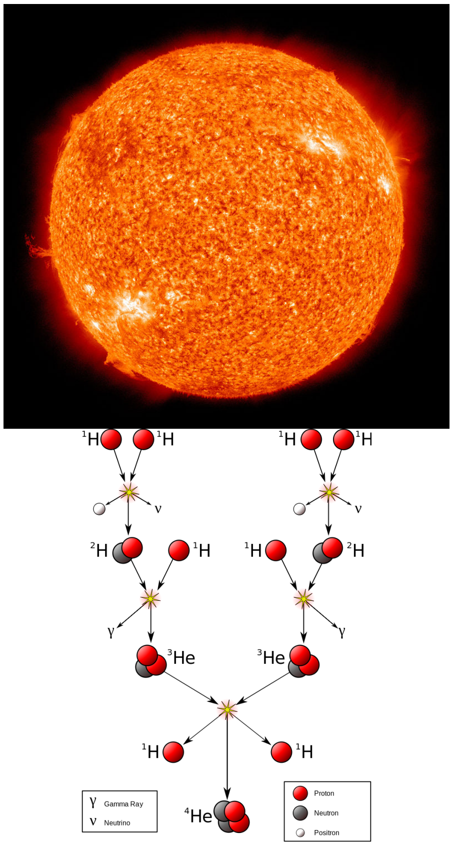


Figure 2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^4_2\text{He} \rightarrow {}^{12}_{6}\text{C}$
b. $6\,{}^1_1\text{H} + 6\,{}^1_0\text{n} \rightarrow {}^{12}_{6}\text{C}$
c. $6\,{}^2_1\text{D} \rightarrow {}^{12}_{6}\text{C}$

Discuss your results.

a. $Q_a = 3 \times 4.0026 - 12.000)\, amu \times (1.4924 \times 10^{-10}\, J/amu) = 1.17 \times 10^{-12}\, J$
b. $Q_b = (6 \times (1.007825 + 1.008665) - 12.00000)\, amu \times (1.4924 \times 10^{1-0} J/amu) = 1.476 \times 10^{-11}\, J$
c. $Q_c = 6 \times 2.014102 - 12.00000\, amu \times (1.4924 \times 10^{-10}\, J/amu) = 1.263 \times 10^{-11}\, J$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

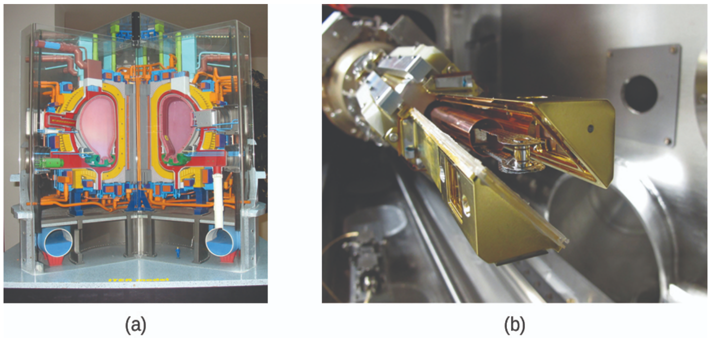

(a)
(b)

Figure 3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world’s largest experimental Tokamak nuclear fusion reactor with a goal of achieving larg\times 10^{scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.Contributors

Contributors

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

2.9 The Nature of Light

Skills to Develop

- To learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves are among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.

Figure 1: A Wave in Water. When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

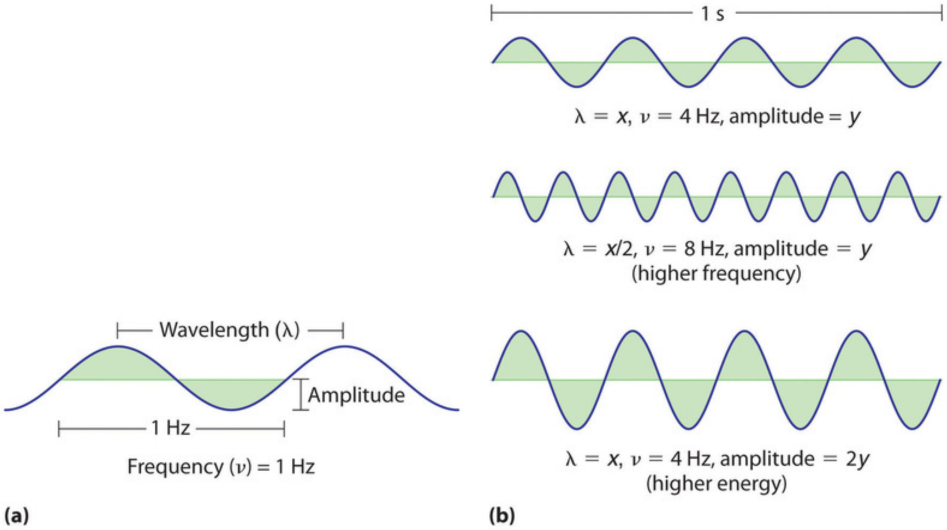


Figure 2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν, in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 2). As you may have noticed in Figure 1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the **wavelength** (λ, lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (ν, lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

The **amplitude**, or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed}onumber \tag{1}$$

$$\lambda\nu = v \tag{2}$$

$$\left(\frac{meters}{\cancel{wave}}\right)\left(\frac{\cancel{\text{wave}}}{\text{second}}\right) = \frac{\text{meters}}{\text{second}} \tag{3}$$

Be careful not to confuse the symbols for the speed, v, with the frequency, ν.

Different types of waves may have vastly different possible speeds and frequencies. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as **electromagnetic radiation**. (Figure 3). Some forms of electromagnetic radiation are shown in Figure 4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458 × 10^8 m/s (about 3.00 ×10^8 m/s or 1.86 × 10^5 mi/s). This is about a million times faster than the speed of sound.

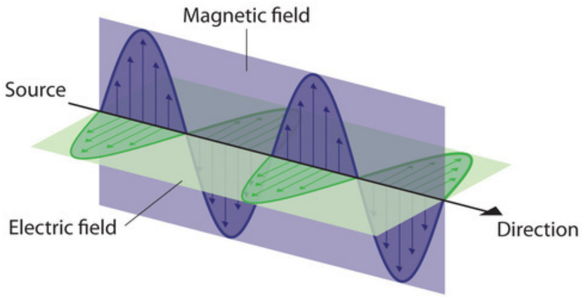


Figure 3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 4 and Table 1, the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with c in Equation2, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda\nu \tag{4}$$

$$\nu = \frac{c}{\lambda} \tag{5}$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7 × 10^{-7} m (700 nm, or 4.3 × 10^{14} Hz) and 4 × 10^{-7} m (400 nm, or 7.5 × 10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly, when frequency decreases, the wavelength increases.

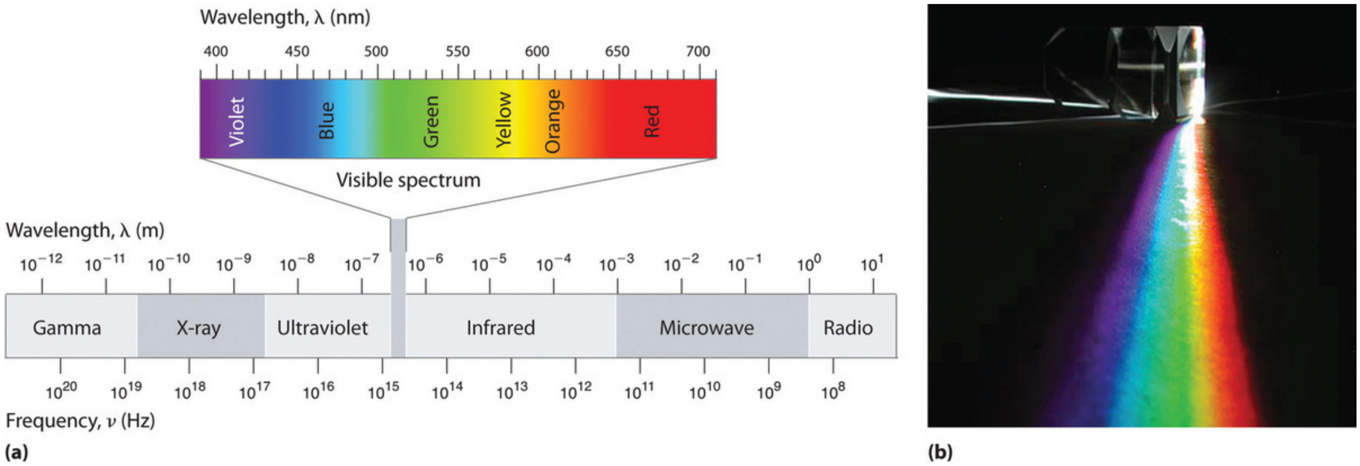


Figure 4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within the visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table* 1*: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	UV, visible
micrometer	µm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^{0}	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \tag{6}$$

$$\propto \frac{1}{\lambda} \tag{7}$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer of the atmosphere absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

> *The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.*

Example 1: Wavelength of Radiowaves

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 5 to calculate the wavelength in meters.

Solution:

From Equation 5, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998 × 10^8 m/s:

$$\begin{aligned} \lambda\nu &= c \\ &= 2.998 \times 10^8 m/s \end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned} \lambda &= \frac{c}{\nu} \\ &= \left(\frac{2.988 \times 10^8\ m/\cancel{s}}{101.1\ \ \cancel{MHz}}\right)\left(\frac{1\ \ \cancel{MHz}}{10^6\ \ \cancel{s^{-1}}}\right) \\ &= 2.965\ m \end{aligned}$$

Exercise 1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Answer

8.45 mm

Light is also Particulate!

We have just spent quite a bit of space describing the wave-like properties of electromagnetic radiation. It turns out, however, that several experimental results showed that light did not always act in a wave-like manner, but instead acted as if it consisted of particles. One of these experimental results involved blackbody radiation. The term “blackbody” was coined by Gustav R. Kirchhoff in 1862. The blackbody radiation curve was known experimentally, but its shape eluded physical explanation until the year 1900. The classical approach to the blackbody radiation problem, known as the Rayleigh-Jeans law, in which radiation is treated as waves (as you have learned above), fails to correctly reproduce experimental results. In the limit of short wavelengths, the classical approach predicts infinite radiation intensity, which is inconsistent with the experimental results in which radiation intensity has finite values in the ultraviolet region of the spectrum. This divergence between the results of classical theory and experiments, which came to be called the ***ultraviolet catastrophe***, shows how classical physics fails to explain the mechanism of blackbody radiation, Figure 5 .

Graph shows the variation of radiation intensity with wavelength. Experimental data depicted as red dots shoots upwards at a wavelength of just under 1 micrometer, climbing to a maximum intensity of around 2 – 3 micrometers, then declining in a curve until almost reaching a baseline at 10. The Rayleigh—Jeans line is shown next to the experimental data line, and is first depicted coming onto the graph at a wavelength of 5 and curving down to almost meet the experimental line around 10.

Figure 5: *The ultraviolet catastrophe: The Rayleigh–Jeans law does not explain the observed blackbody emission spectrum.*

The blackbody radiation problem was solved in 1900 by Max **Planck**. The innovative idea that Planck introduced in his model is the assumption that electromagnetic radiation must exist as individual packets of energy, which he called quanta. Planck related the energy of electromagnetic radiation to its frequency by the equation

$$E = h \times \nu \tag{8}$$

In Equation 8, ν is the frequency of the electromagnetic radiation. The physical constant h is called ***Planck's constant***:

$$h = 6.626 \times 10^{-34} J \cdot s \tag{9}$$

Planck's blackbody radiation law is in agreement with the experimental blackbody radiation curve (Figure 6):

Graph shows the variation of radiation intensity with wavelength. Experimental data, red dots, show the maximum around 2 – 3 micrometers. Planck fit, line, perfectly matches experimental data.

***Figure 6**: Planck's theoretical result (continuous curve) and the experimental blackbody radiation curve (dots).*

When Planck first published his result, the hypothesis of an energy quantum was not taken seriously by the physics community because it did not follow from any established physics theory at that time. It was perceived, even by Planck himself, as a useful mathematical trick that led to a good theoretical "fit" to the experimental curve. This perception was changed in 1905 when Einstein published his explanation of the photoelectric effect, another experiment that was best explained if electromagnetic radiation was acting as individual particles. In Einstein's explanation of the photoelectric effect, he gave Planck's energy quantum a new meaning: that of a particle of light. Einstein also gave a new name to Planck's quantum of electromagnetic energy: a **photon**.

The concept of the photon had emerged from experimentation with *thermal blackbody radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In the next section, we describe how observation of the interaction of individual atoms with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a line spectrum, are observed rather than a continuous range of wavelengths (Figure 6). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

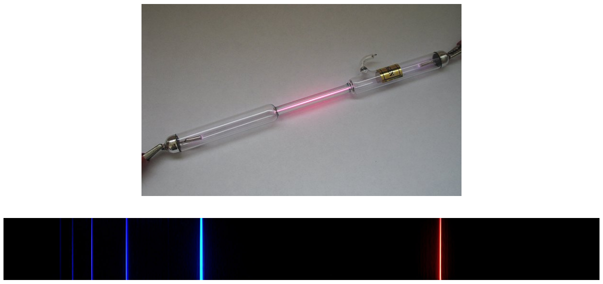


Figure 6: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

Bohr's Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 7). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

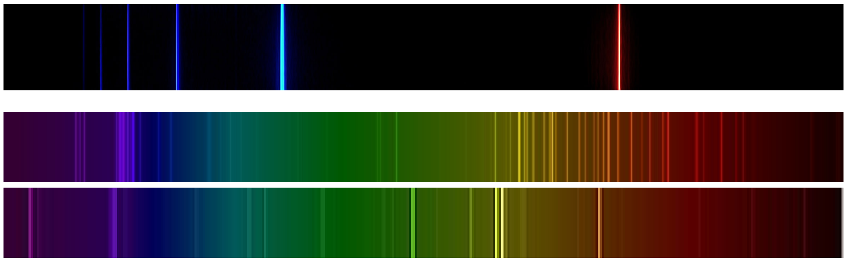


Figure 7: *The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.*

Summary

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength** (λ), the distance between successive waves; **frequency** (u), the number of waves that pass a fixed point per unit time; **speed** (v), the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light** (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Contributors

- Modified by Joshua Halpern (Howard University)
- Modified by Tom Neils (Grand Rapids Community College)

2.10 Quantum Mechanics and The Atom

Skills to Develop

- To apply the results of quantum mechanics to chemistry.

The wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x, y, and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy E. The properties of wavefunctions derived from quantum mechanics are summarized here:

- **A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x, y, and z), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 6.5.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

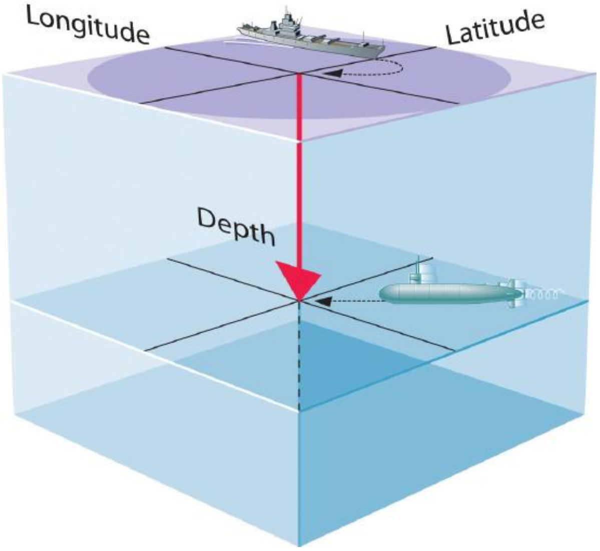


***Figure* 1**: *The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object*

- **The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wavefunction (Ψ^2) is proportional to the probability of finding an electron at a given point. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 2.

- **Each wavefunction is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

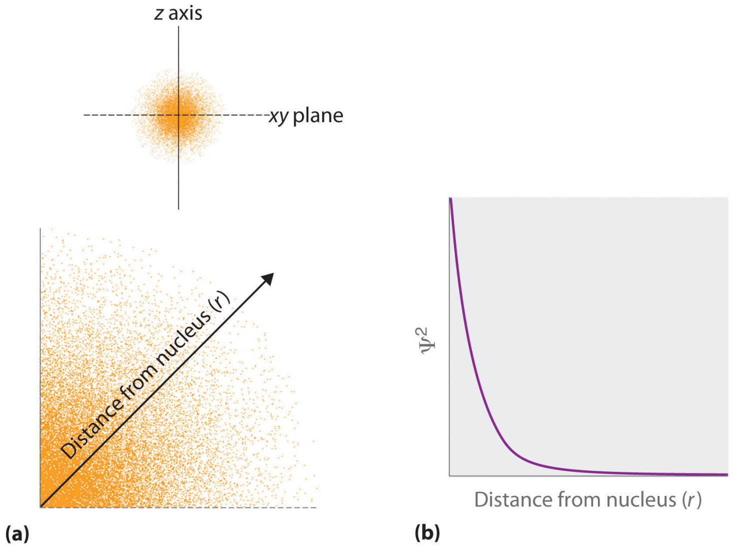


Figure 2: *Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at r = 0 (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but not zero.*

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n, l, and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and m_l are allowed for a given value of n.

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \dots \tag{1}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number (l)**. The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n - 1$:

$$l = 0, 1, 2, \dots, n-1 \tag{2}$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l+1, \ldots, 0, \ldots, l-1, l \tag{3}$$

For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be −1, 0, or +1; and if $l = 2$, m_l can be −2, −1, 0, +1, or +2.

Each wavefunction with an allowed combination of n, l, and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example1: n=4 Shell Structure

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A. Given $n = 4$, calculate the allowed values of l. From these allowed values, count the number of subshells.
B. For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

Exercise 1: n=3 Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer

three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: sharp, principle, diffuse, and fundamental.) A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has *n* subshells. For *n* = 1, only a single subshell is possible (1*s*); for *n* = 2, there are two subshells (2*s* and 2*p*); for *n* = 3, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with *n* ≥ 2 also has an *np* subshell, and any shell with *n* ≥ 3 also has an *nd* subshell. Because a 2*d* subshell would require both *n* = 2 and *l* = 2, which is not an allowed value of *l* for *n* = 2, a 2*d* subshell does not exist.
- Each subshell has 2*l* + 1 orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

> *Each principal shell has n subshells, and each subshell has 2l + 1 orbitals.*

Table* 1*: *Values of n, l, and ml through n = 4*

n	**l**	**Subshell Designation**	m_l	**Number of Orbitals in Subshell**	**Number of Orbitals in Shell**
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Skills to Develop

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr’s orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of containing an electron.

One way of representing electron probability distributions was illustrated previously for the 1*s* orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is very small but *not* zero.

In contrast, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius $r_1, r_2, r_3, \ldots, r_{x-1}, r_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure 1*a*), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (Figure 1*b*), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure 1*c*). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure 1*d*). Most important, when r is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure 1*d*).

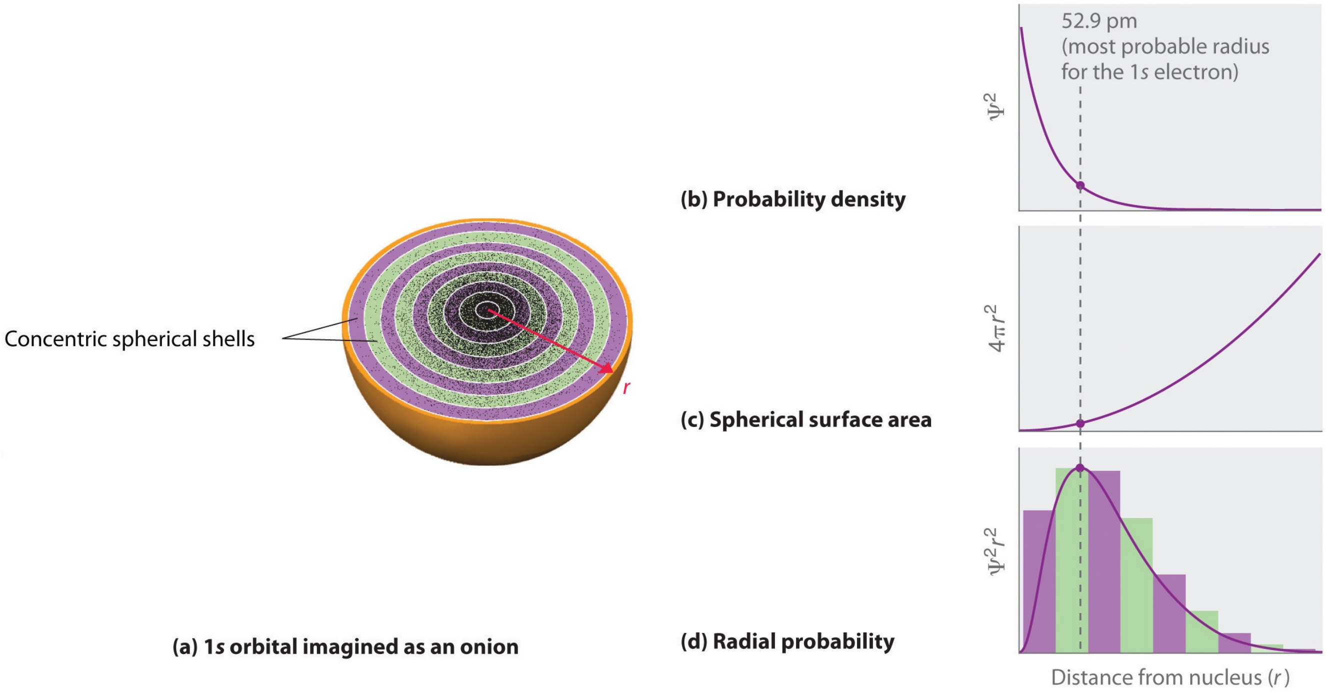
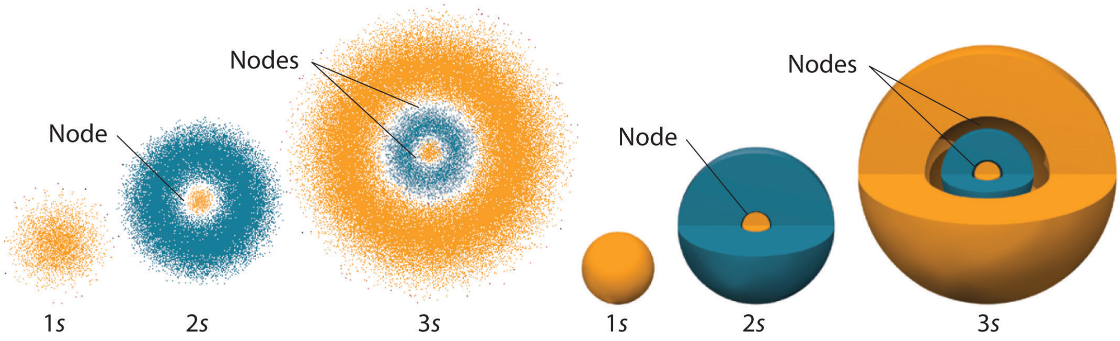


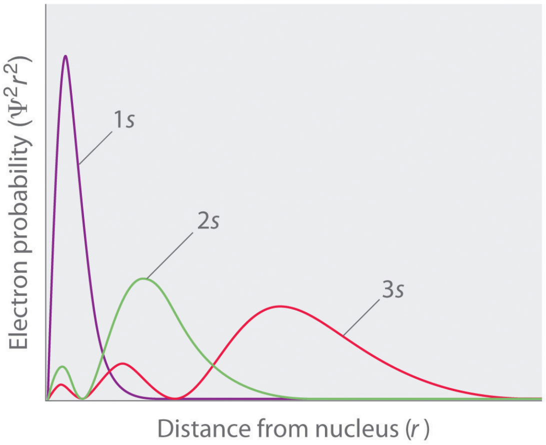
***Figure* 1**: *Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density* Ψ^2 *versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by* $4\pi r^2$*, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.*

For the hydrogen atom, the peak in the radial probability plot occurs at $r = 0.529$ Å (52.9 pm), which is exactly the radius calculated by Bohr for the $n = 1$ orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 2 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (Figure 2*c*). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave *phase* in the wavefunction Ψ.



(a) Electron probability **(b) Contour probability**



(c) Radial probability

***Figure 2**: Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r.*

s Orbitals (l=0)

Three things happen to *s* orbitals as *n* increases (Figure 2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals (l=1)

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has *l* = 1, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals.

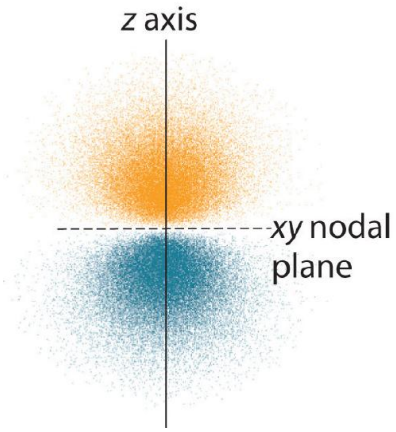


Figure 3: *Electron Probability Distribution for a Hydrogen 2p Orbital. The nodal plane of zero electron density separates the two lobes of the 2p orbital. As in Figure 2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).*

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 3. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 4, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each *p* orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

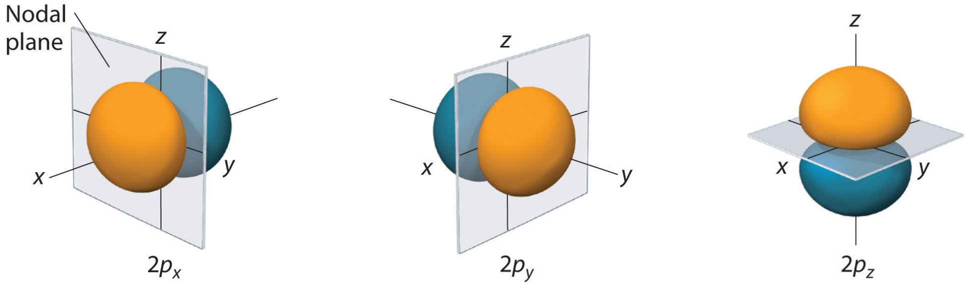


Figure 4 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative. Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 4.

d Orbitals (l=2)

Subshells with *l* = 2 have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to *n* = 3. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2.

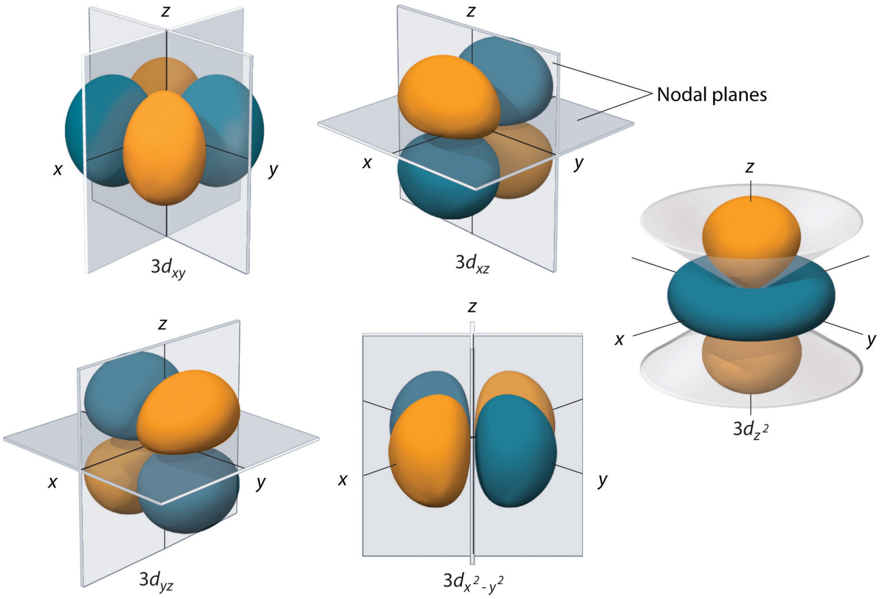


Figure 5: *The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital,* $3d_{z^2}$*, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.*

The hydrogen 3d orbitals, shown in Figure 5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, \)3d_{xz}\), and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 5.

f Orbitals (l=3)

Principal shells with *n* = 4 can have subshells with *l* = 3 and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex. Because *f* orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of *l* are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with *n* ≤ 4 for a hydrogen atom are plotted in Figure 6; note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of *n* (e.g., the three 2*p* orbitals) are **degenerate**, meaning that they have the same energy. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure 6 shows that the energy levels become closer and closer together as the value of *n* increases, as expected because of the $1/n^2$ dependence of orbital energies.

Figure 6: *Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.*

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation, which can be extended to other single-electron species by incorporating the nuclear charge *Z* (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} Rhc \tag{4}$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Summary

There is a relationship between the locations of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions (Ψ)** to describe the mathematical relationship between the location of electrons in atoms and molecules and their energies. Wavefunctions have four important properties:

1. the wavefunction uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron;
2. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
3. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and

4. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. wavefunctions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

The four chemically important types of atomic orbital correspond to values of $\ell = 0, 1, 2,$ and 3. Orbitals with $\ell = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $ell = 0$ contain one or more nodes. Orbitals with $\ell = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Contributors

- Modified by Joshua Halpern (Howard University)
- Modified by Tom Neils (Grand Rapids Community College)

2.11 Trends of the Periodic Table

Skills to Develop

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group VIA (16), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, (3) electron affinities, (4) electronegativities, and (5) the number of valence electrons.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).

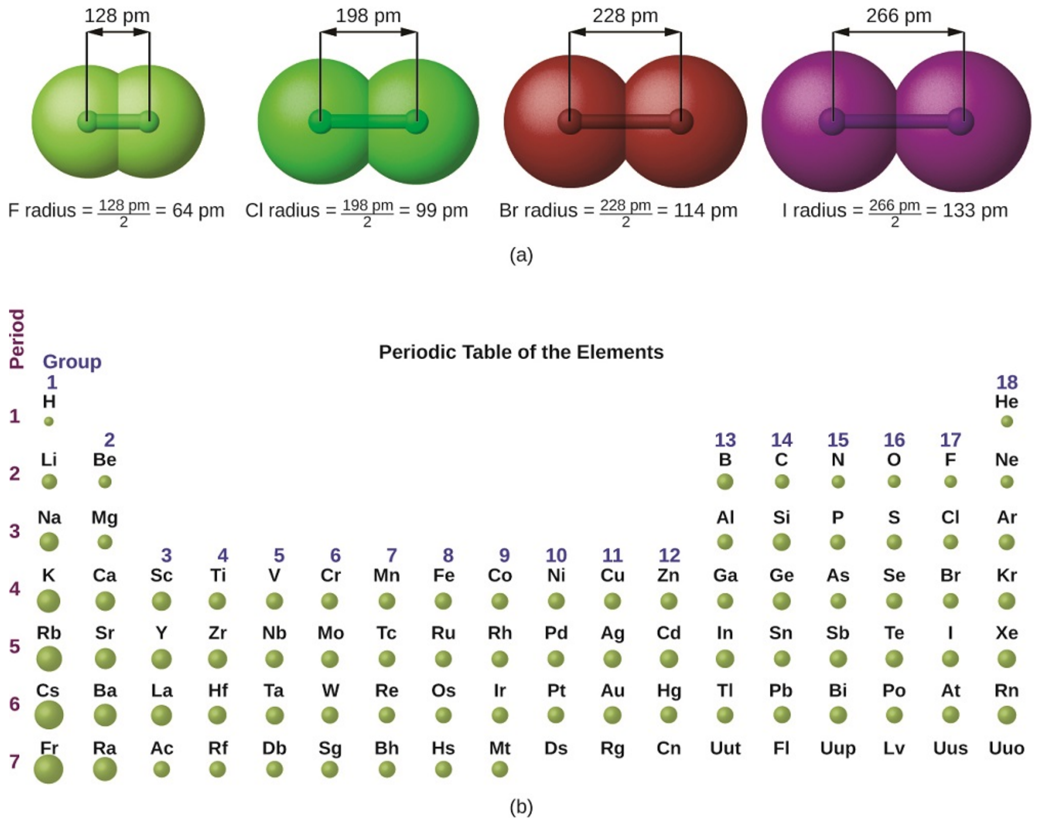


Figure* 1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.*

We know that as we move down a group, the principal quantum number, n, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 1 and Figure 1. The trends for the entire periodic table can be seen in Figure 2.

Table* 1*: Covalent Radii of the Halogen Group Elements

Atom	**Covalent radius (pm)**	**Nuclear charge**
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure 2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This trend can be explained with the concept of effective nuclear charge, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - shielding \tag{1}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

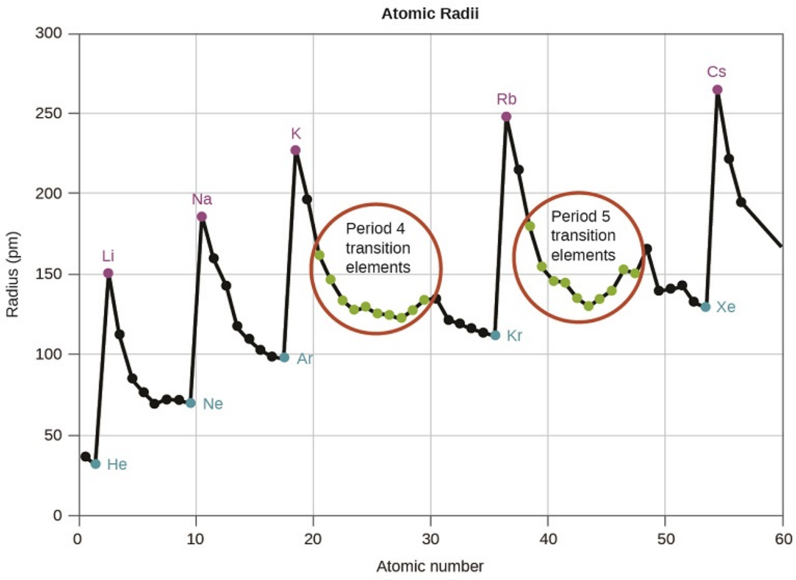


Figure 2: *Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.*

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *s* or *p* electrons that are farthest from the nucleus.

Example 1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Exercise 1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$X(g) \longrightarrow X^{+}(g) + e^{-} \qquad IE_1 \tag{2}$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$X^{+}(g) \longrightarrow X^{2+}(g) + e^{-} \qquad IE_2 \tag{3}$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farthest from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

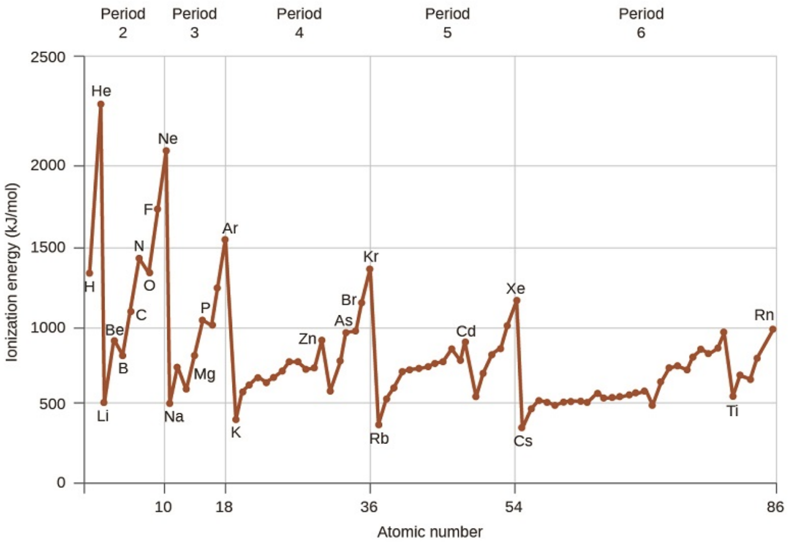
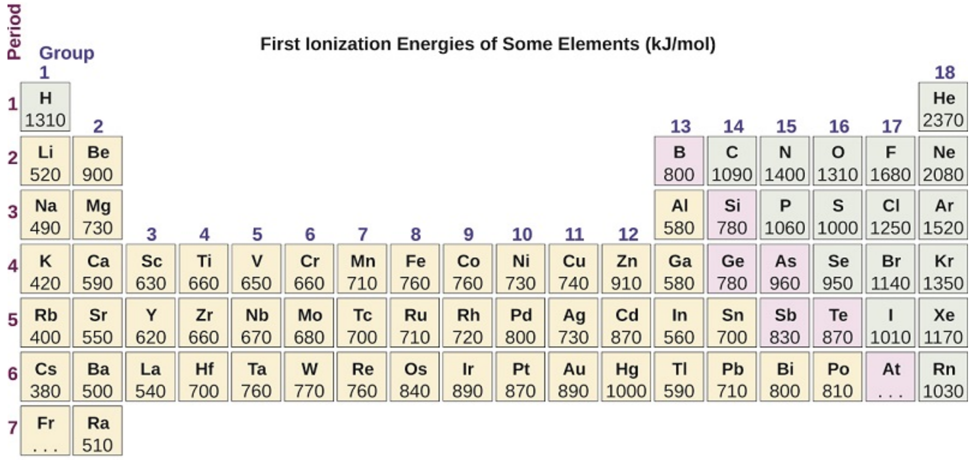


***Figure 4**: The first ionization energy of the elements in the first five periods are plotted against their atomic number.*

Figure 4 graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however we will not attempt to explain them in this course.



First Ionization Energies of Some Elements (kJ/mol)

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1310																	He 2370
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

***Figure 5**: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements.*

Example 2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for F, IE_1 for Se, IE1 for N, IE1 for At.

Solution

Removing the highest energy electron requires less energy the farther an electron is away from the nucleus. The size of the atoms is At > Se > N > F, so the IE trend is the reverse:

$$IE_1(At) < IE_1(Se) < IE_3(N) < IE_2(F).$$

Exercise 2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

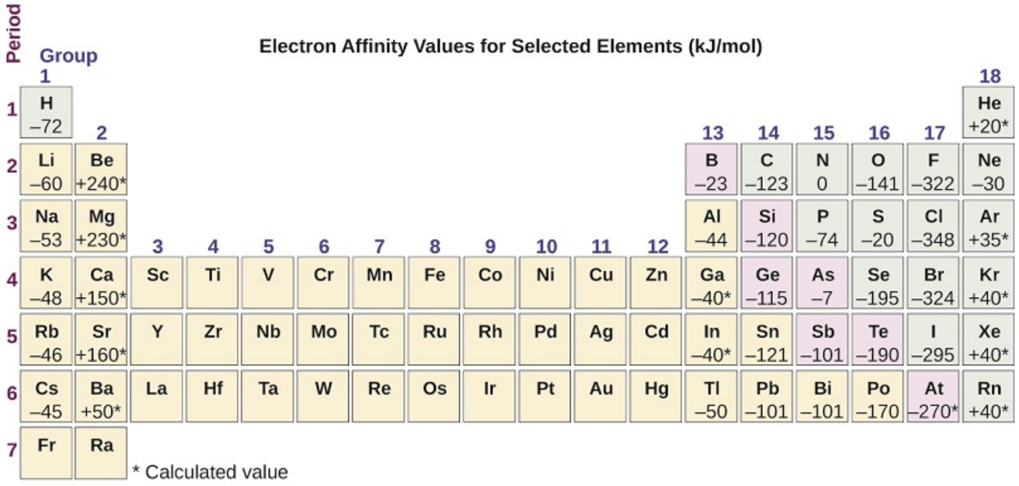
Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$\mathrm{X}(g)+\mathrm{e}^{-}\longrightarrow \mathrm{X}^{-}(g)\qquad \mathrm{EA}_1 \tag{4}$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. There are good explanations for the variations in EA, but we will not discuss them in this class.

Just as with ionization energy, subsequent EA values are associated with forming ions with greater charges. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.



Electron Affinity Values for Selected Elements (kJ/mol)

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –20	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

The properties discussed in this section (size of atoms, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Variation in Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity**, defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom's electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for assigning the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive, for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 4.09), thereby creating a scale in which all elements have values between 0 and 4.0.

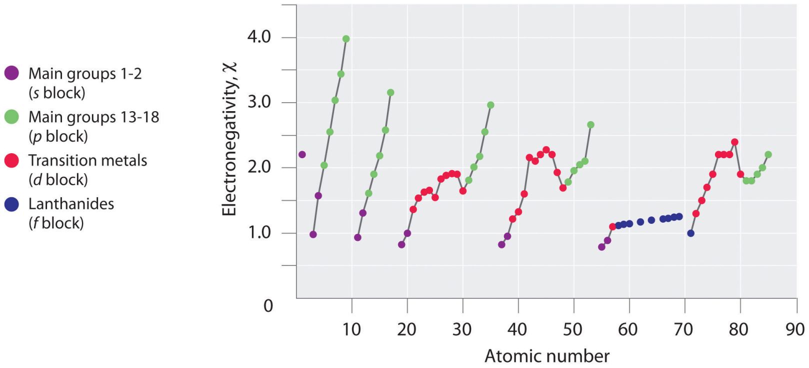


Figure 1: *A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table*

Periodic variations in Pauling's electronegativity values are illustrated in Figures 1 and 2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br). It is very important to note that the electronegativity of H is similar to that of C.

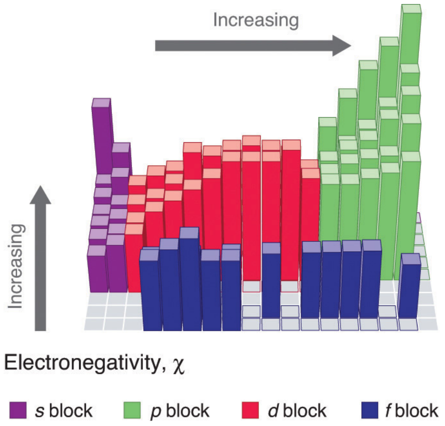
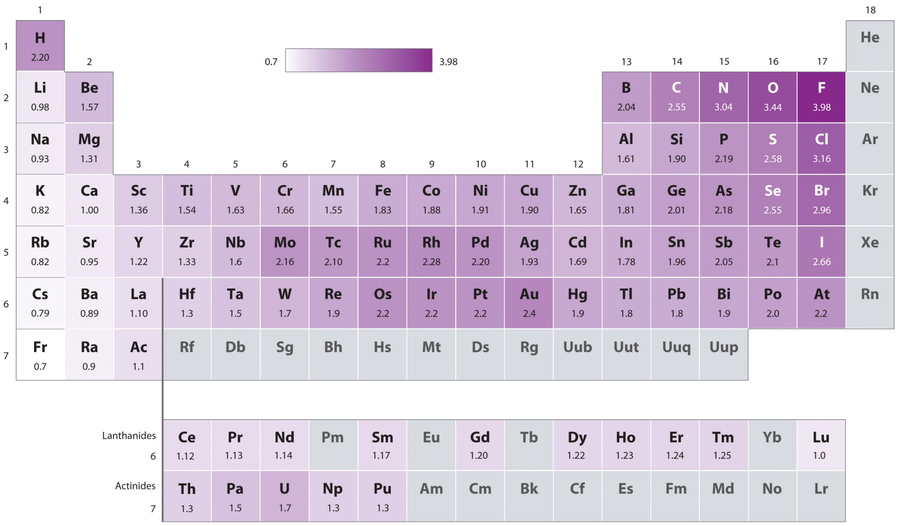


Figure 2: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd*

ed. (1960).

Linus Pauling (1901-1994)

When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school, but was later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity (\ ≥ 2.2 in Figure 2) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity (≤ 1.8) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities (~ 2.0). These are the **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

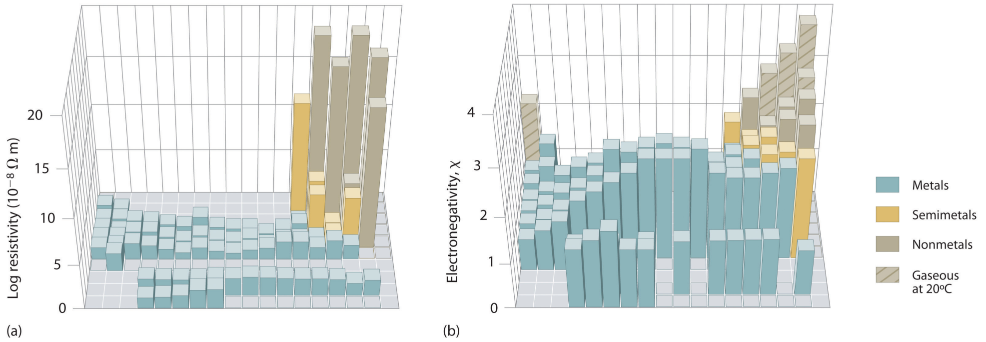


Figure 3: *Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).*

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond polarities, and the kinds of reactions that compounds undergo.

Example 1: Increasing Electronegativity

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

Exercise 1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

Number of Valence Electrons

One last trend that occurs on the periodic table is the trend of the number of **valence electrons**, which are the electrons that are farthest from the nucleus, and thus are the electrons that have the most energy, and that are involved in chemical reactions. For the A Group elements (IA-VIIIA), the the valence electrons are those electrons in the *s* and *p* subshells of the highest energy shell. Conveniently, the number of valence electrons for the A Group elements is equal to the group number. Thus, Na in Group IA has 1 valence electron, whereas C, in Group IVA has 4 valence electrons.

Summary

The arrangement of electrons in atoms allows us to understand many periodic trends. Covalent radius increases as we move down a group because the electrons are located in *shells* that are further from the nucleus. Covalent radius mostly decreases as we move left to right across a period because the electrons are pulled in more tightly to the nucleus. Ionization energy (IE, the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger atom. Electron affinity (EA, the energy associated with forming an anion) has no simply-explained trends. Electronegativity (EN) is *defined as the relative* ability of an atom to attract electrons to itself *in a chemical compound*. Fluorine has been assigned the highest EN value and the EN values of other elements decrease the farther they are from fluorine.

Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy required to add an electron to a gaseous atom to form an anion

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic

group of ions or atoms that have identical electron configurations

Contributors

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

2.12 Example Problems

1. Atomic Structure Problems

1. What is the difference between a gram and an atomic mass unit (a.k.a. a Dalton)?

2. What makes all barium (Ba) atoms different from all atoms of any other element?

3. Isotopes always have different densities. Why is this?

4. Write the nuclide symbol for the following particles:

  a) a copper atom with 35 neutrons and 27 electrons

  b) a sulfur atom with 15 neutrons and 17 electrons

5. What is the weighted average mass of potassium if the three major isotopes are K-39 with a mass of 38.96371 amu and an abundance of 93.1%; K-40 with a mass of 39.974 amu and an abundance of 0.00118%; K-41 with a mass of 40.96184 and an abundance of 6.88%?

Exercise 1

Answers to Q 1-5

Answer

1. A gram is a mass unit useful for the macroscopic scale. An amu is a mass unit appropriate for the atomic scale because 1.0000 amu is 1.6605 x 10^{-24} grams.

2. All barium atoms have 56 protons, and all atoms with 56 protons are barium atoms.

3. Isotopes differ by the number of neutrons. the neutrons exist in the nucleus of an atom, and changing the size of the nucleus does not change the size of the atom. Thus isotopes have different masses, but their volumes are the same, meaning they have different densities.

4. a) ${}^{64}_{29}Cu^{2+}$ b) ${}^{31}_{16}S^{1-}$

5. (38.96371)(.931) + (39.974)(0.0000118) + (40.96184)(0.0688) = 39.09 amu

2. The Mole

6. How many moles of sodium atoms (Na) are there in 43.6 grams of sodium atoms?

7. How many grams of argon (Ar) are there in 134 grams of argon atoms?

8. What is the mass, in grams, of 0.675 moles of radium (Ra) atoms?

9. What is the mass, in grams, of 9.64 x 10^{23} osmium (Os) atoms?

Exercise 2

Answers to Q 6-9

Answer

6. $43.6\ grams\ Na\ atoms x \frac{1\ mole\ Na\ atoms}{22.99\ grams\ Na\ atoms}$ = 1.90 grams Na atoms

7. $134\ grams\ Ar\ atoms x \frac{1\ mole\ Ar\ atoms}{39.85\ grams\ Ar\ atoms} x \frac{6.022x10^{23}\ Ar\ atoms}{1\ mole\ Ar\ atoms}$ = 2.02x10^{24} Ar atoms

8. $0.675\ moles\ Ra\ atoms x \frac{226\ grams\ Ra\ atoms}{1\ mole\ Ra\ atoms}$ = 153 grams Ra atoms

9. $9.64x10^{23}\ Os\ atoms x \frac{1\ mole\ Os\ atoms}{6.022x10^{23}\ Os\ atoms} x \frac{190.23\ grams\ Os\ atoms}{1\ mole\ Os\ atoms}$ = 305 grams Os atoms.

3. Nuclear Reactions

10. Determine the nuclide symbol for the missing particle in the following nuclear reactions:

a) ${}^{35}_{16}S + {}^{4}_{2}He \rightarrow {}^{18}_{9}F + ?$

b) ${}^{139}_{56}Ba \rightarrow {}^{0}_{-1}\beta + ?$

c) ${}^{90}_{38}Sr + {}^{182}_{75}Re \rightarrow 2{}^{1}_{0}n + ?$

11. If you start with 25.00 grams of a radioactive nuclide, X, how many grams of X will remain after 3 half-lives?

12. If you start with 37.3 grams of radioactive nuclide X, how many hours will it take until there are only 10.0 grams of X? The half-life of X is 17.1 hours.

Exercise 3

Answers to Q 10-12

Answer

10. a) ${}^{21}_{9}F$ b) ${}^{139}_{57}La$ c) ${}^{270}_{113}Nh$

11. 25.00 → 12.50 → 6.250 → 3.125 g or $(1/2)^3$(25.00 grams) = 3.125 grams

12. $10.0g = (1/2)^n(37.3g) \Rightarrow \frac{10.0}{37.3} = (1/2)^n \Rightarrow \frac{log(0.2681)}{log(0.5)}$ = n = 1.899 half-lives. 1.899 x 17.1 hours = 32.5 hours.

4. Electronic Structure

13. Which has the greater energy per photon, green light or red light?

14. What does an atomic orbital boundary surface tell you?

15. Tell the maximum number of electrons possible in:

a) a 1s orbital

b) a 5d orbital

c) a 2p subshell

d) a 4d subshell

e) shell 3

16. Compare a Ca atom and an Se atom in terms of

a) atomic size

b) ionization energy

c) electronegativity

d) number of valence electrons

Exercise 4

Answers to Q 13-16

Answer

13. Energy is directly proportional to the frequency, and green light has a higher frequency than red light, so green photons have higher energy than red photons.

14. An atomic orbital boundary surface tells the volume of space in which an electron can be found 90% of the time.

15. a) 2 b) 2 c) 6 d) 10 e) 18

16. A Ca atom a) is larger than a Se atom b) has a lower first I.E. than a Se atom c) has a lower EN than a Se atom d) has fewer valence electrons than a Se atom.

Modified by Tom Neils (Grand Rapids Community College)

CHAPTER OVERVIEW

3: Chemical Formulas and Bonding

3.1 An Atomic-Level Perspective of Ionic and Covalent Compounds

Skills to Develop

- 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 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 1).

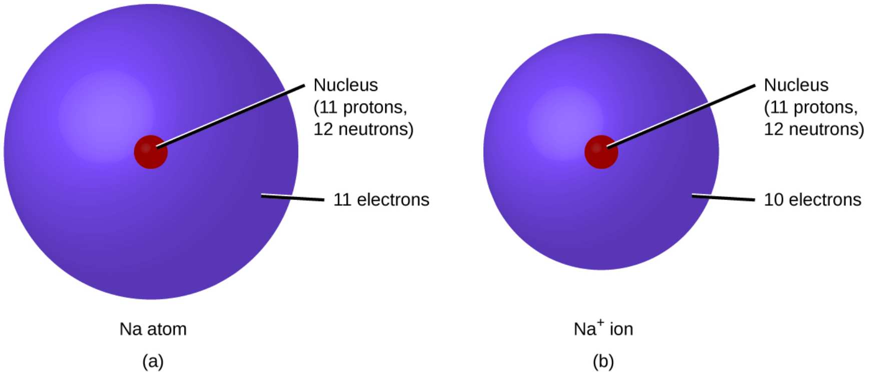


***Figure 1**: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.*

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 IA) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group IIA) 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 VIIA gain one electron and form anions with a 1− charge; atoms of group VIA 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 (an octet of valence electrons) reflected in these predictive rules for ion formation exists, but is not is described in this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 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 IA elements form 1+ ions; group IIA 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 VIIA elements (one group left of the noble gases) form 1− ions; group VIA elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

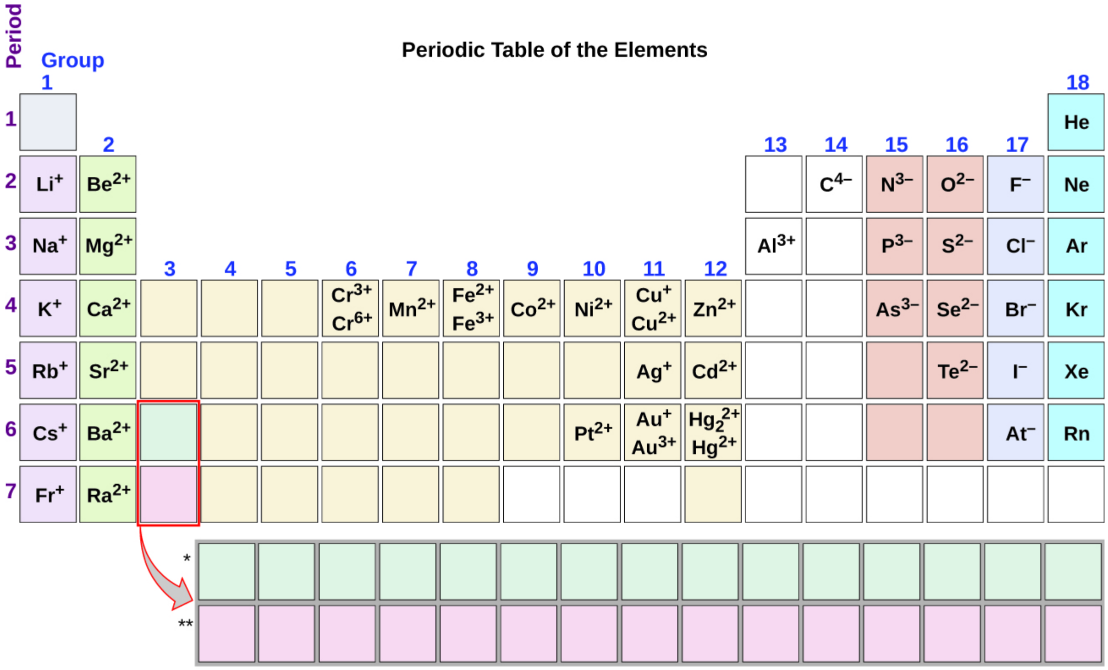


Figure 2: *Some elements exhibit a regular pattern of ionic charge when they form ions.*

Example 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 1

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

Answer

Se^{2-}, the selenide ion

Example 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 IIA) 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 VA) 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 2

Aluminum and chlorine 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. Chlorine will form an anion with a charge of 1−: Cl^{-}, a chloride 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 a group of covalently-bonded atoms with an overall charge. Some of the more important polyatomic ions are listed in Table 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* 1*: *Common Polyatomic Ions*

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}	hydroxide	OH^-
peroxide	O_2^{2-}		
hydroxide	OH^-	water	H_2O
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
cyanate	OCN^-	cyanic acid	$HOCN$
carbonate	CO_3^{2-}	hydrogen carbonate	HCO_3^-
hydrogen carbonate	HCO_3^-	carbonic acid	H_2CO_3
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	hydrogen sulfate	HSO_4^-
hydrogen sulfate	HSO_4^-	sulfuric acid	H_2SO_4
sulfite	SO_3^{2-}	hydrogen sulfite	HSO_3^-
hydrogen sulfite	HSO_3^-	sulfurous acid	H_2SO_3
phosphate	PO_4^{3-}	hydrogen phosphate	HPO_4^{2-}
hydrogen phosphate	HPO_4^{2-}	dihydrogen phospahte	$H_2PO_4^-$
dihydrogen phosphate	$H_2PO_4^-$	phosphoric acid	H_3PO_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 module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

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

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

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).

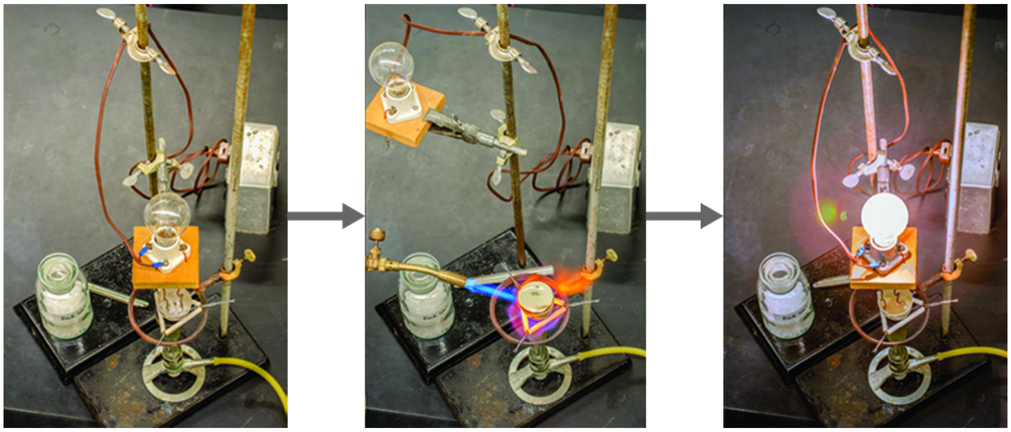


Figure 3: *Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)*

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

Example 3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 4) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Figure 4: *Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)*

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

Exercise 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 1) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $\left(PO_4^{3-}\right)$ groups. The 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 4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4^-$. 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 $H_2PO_4^-$ 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 4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, 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 cannot be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Molecular Compounds

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

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

Example 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 IA) is a metal, and iodine (group VIIA) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group IA) is a nonmetal, and oxygen (group VIA) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group IVA) is a nonmetal, hydrogen (group IA) is a nonmetal, and chlorine (group VIIA) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group IA) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Exercise 5

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

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

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

Summary

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

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

Glossary

covalent bond

attractive force between the nuclei of a molecule’s atoms and pairs of electrons between the atoms

covalent compound

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

ionic bond

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

ionic compound

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

molecular compound

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

monatomic ion

ion composed of a single atom

polyatomic ion

ion composed of more than one atom

oxyanion

polyatomic anion composed of a central atom bonded to oxygen atoms

Contributors

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

3.2 Composition of Compounds

Skills to Develop

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

Chemistry is the experimental and theoretical study of materials at both the macroscopic and microscopic levels. Understanding the relationship between properties and structures/bonding is a major aspect of these theoretical and experimental studies. A chemical formula is a format used to express the structure of compounds. The formula tells which elements and how many of each element are present in a compound. Formulas are written using the elemental symbol of each atom and a subscript to denote the number of elements.

Molecular formulas tell you how many atoms of each element are in a compound, and **empirical formulas** tell you the simplest or most reduced ratio of elements in a compound. If a compound's molecular formula cannot be reduced any more, then the empirical formula is the same as the molecular formula. Once the molar mass of the compound is known, the molecular formula can be calculated from the empirical formula.

Formulas on the Atomic and the Molar Level

A chemical formula tells us the relative ratios of different atoms in a compound. The ratios hold true on the *molar* level as well as the *atomic* level. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. One molecule of water has a mass of 18.02 amus. Likewise, 1.000 **mole** of H_2O molecules is composed of 2.000 **moles** of hydrogen and 1.000 **mole** of oxygen. The mass of 1.000 **mole** of water molecules has a mass of 18.02 grams.

Example 1: Acetone

An acetone molecule has the chemical formula of C_3H_6O.

Questions:

a) Is C_3H_6O an empirical formula, a molecular formula, or both?

b) How many H atoms are in one acetone molecule?

c) How many total atoms are in one acetone molecule?

d) What is the mass, in amus, of one acetone molecule?

e) What is the mass, in grams, of 1.000 mole of acetone molecules?

f) How many H atoms are in 1.000 mole of acetone molecules?

g) How many total atoms are in 1.000 mole of acetone molecules?

Solutions:

a) The formula is both an empirical formula (because it is the simplest ratio of elements) and also a molecular formula (because the formula tells the actual number of atoms of each element in one acetone molecule).

b) There are 6 H atoms in one acetone molecule.

c) There are 10 total atoms (6 H + 3 C + O) in one acetone molecule.

d) The mass of one acetone molecule: $6\ H\ atoms \times \frac{1.008\ amus}{H\ atom} + 3\ C\ atoms \times \frac{12.01\ amus}{C\ atom} + 1\ O\ atom \times \frac{16.00\ amus}{O\ atom} = 58.08 amus$

e) The mass of 1.000 mole of acetone molecules:

$$6\ moles\ H\ atoms \times \frac{1.008\ grams}{1.000\ moles\ H\ atoms} + 3\ moles\ C\ atoms \times \frac{12.01\ grams}{1.000\ moles\ C\ atoms} + 1\ mole\ O\ atoms \times \frac{16.00\ grams}{1.000\ mole\ O\ atoms} = 58.08 grams \tag{1}$$

f) H atoms in 1.00 mole of acetone molecules:

$$1.000\ mole\ acetone\ molecules \times \frac{6\ moles\ H\ atoms}{\begin{array}{c}1.000\ mole\ acetone\ molecules\\ atoms\end{array}} \times \frac{6.022x10^{23}\ H\ atoms}{1.000\ moles\ H\ atoms} = 3.613x10^{24} H \tag{2}$$

g) Total atoms in 1.000 moles of acetone molecules:

$$1.000\ mole\ acetone\ molecules \times \frac{10\ moles\ atoms}{1.000\ mole\ acetone\ molecules} \times \frac{6.022x10^{23}\ atoms}{1.000\ mole\ atoms} = 6.022x10^{24}\ atoms \tag{3}$$

Exercise 1

An certain molecule has the chemical formula of $C_8H_8O_4$

Questions:

a) Is $C_8H_8O_4$ an empirical formula, a molecular formula, or both?

b) How many H atoms are in one $C_8H_8O_4$ molecule?

c) How many total atoms are in one $C_8H_8O_4$ molecule?

d) What is the mass, in amus, of one $C_8H_8O_4$ molecule?

e) What is the mass, in grams, of 1.000 mole of $C_8H_8O_4$ molecules?

f) How many H atoms are in 1.000 mole of $C_8H_8O_4$ molecules?

g) How many total atoms are in 1.000 mole of $C_8H_8O_4$ molecules?

Answer

a) The formula is a molecular formula, because it is **<u>not</u>** the simplest ratio of elements. The empirical formula is $C_2H_2O_1$

b) There are 8 H atoms in one acetone molecule.

c) There are 20 total atoms (8 H + 8 C + 4 O) in one $C_8H_8O_4$ molecule.

d) The mass of one $C_8H_8O_4$ molecule: $8\ H\ atoms \times \frac{1.008\ amus}{H\ atom} + 8\ C\ atoms \times \frac{12.01\ amus}{C\ atom} + 4\ O\ atom \times \frac{16.00\ amus}{O\ atom} = 168.1 amus$

e) The mass of 1.000 mole of $C_8H_8O_4$ molecules:

$$8\ moles\ H\ atoms \times \frac{1.008\ grams}{1.000\ moles\ H\ atoms} + 8\ moles\ C\ atoms \times \frac{12.01\ grams}{1.000\ moles\ C\ atoms} + 4\ mole\ O\ atoms \times \frac{16.00\ grams}{1.000\ mole\ O\ atoms} = 168.1 grams \tag{4}$$

f) H atoms in 1.00 mole of $C_8H_8O_4$ molecules:

$$1.000\ mole\ C_8H_8O_4\ molecules \times \frac{8\ moles\ H\ atoms}{1.000\ mole\ C_8H_8O_4\ molecules} \times \frac{6.022x10^{23}\ H\ atoms}{1.000\ moles\ H\ atoms} = 4.818x10^{24} H\ atoms \tag{5}$$

g) Total atoms in 1.000 moles of $C_8H_8O_4$ molecules:

$$1.000\ mole\ C_8H_8O_4\ molecules \times \frac{20\ moles\ atoms}{1.000\ mole\ C_8H_8O_4\ molecules} \times \frac{6.022x10^{23}\ atoms}{1.000\ mole\ atoms} = 1.204x10^{25}\ atoms \tag{6}$$

Structural Formulas

There are several ways to write and draw chemical formulas for covalently-bonded compounds, depending on how much information about the structure is needed.

Condensed Structural Formula

Condensed structural formulas show a bit more information about the bonding order of atoms in a molecule than a simple molecular formula. A condensed structural formula is written in a single line to save space and make it more convenient and faster to write out. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together.

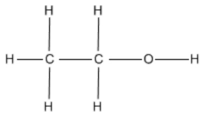
Ex. Condensed Structural Formula for ethanol: CH_3CH_2OH (molecular Formula: C_2H_6O).

Condensed Structural Formula for dimethyl ether: $(CH_3)_2O$ (molecular formula: C_2H_6O).

Expanded Structural Formula

A structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. Structural formulas are helpful because they explain the properties and structure of the compound which condensed formulas cannot always represent.

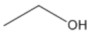
Structural Formula for CH_3CH_2OH, ethanol



Line-Angle Formula

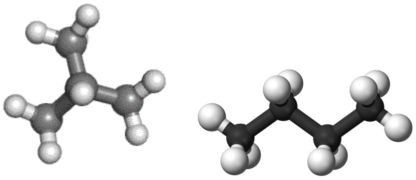
Because organic compounds can be complex, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by omitting the symbol of H atoms attached to C atoms, and by replacing the C element symbols with the intersection of lines. Thus, a carbon atom is present wherever one line intersects another line. Hydrogen atoms are assumed to complete each of carbon's four bonds. All other atoms that are connected to carbon atoms are written out. Line angle formulas help show structure and order of the atoms in a compound making the advantages and disadvantages similar to structural formulas.

Line-Angle Formula for Ethanol:



Isomers

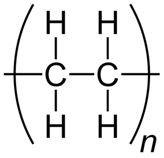
Understanding how atoms in a molecules are arranged and how they are bonded together is very important in giving the molecule its identity. Isomers are compounds in which two molecules have the same number of atoms, and thus the same molecular formula, but have completely different physical and chemical properties because of differences in structural formula.



Methylpropane and butane have the same molecular formula of C_4H_{10}, but are structurally different (methylpropane on the left, butane on the right).

Polymers

A polymer is formed when small molecules of identical structure, monomers, combine into a large cluster. The monomers are joined together by covalent bonds. When monomers repeat and bind, they form a polymer. While they can be comprised of natural or synthetic molecules, polymers often include plastics and rubber. When a molecule has more than one of these polymers, parenthesis are used to show that all the elements within the polymer are multiplied by the subscript outside of the parenthesis. The subscript (shown as n in the example below) denotes the number of monomers present in the macromolecule (or polymer).



Ethylene becomes the polymer polyethylene.

O

Contributors

- Mike Blaber (Florida State University)
- Modified by Tom Neils (Grand Rapids Community College)

3.3 Chemical Bonds

Skills to Develop

- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Chemical bonds form when electrons can be simultaneously close to two or more nuclei, but beyond this, there is no simple, easily understood theory that would not only explain why atoms bind together to form molecules, but would also predict the three-dimensional structures of the resulting compounds as well as the energies and other properties of the bonds themselves. Unfortunately, no one theory exists that accomplishes these goals in a satisfactory way for all of the many categories of compounds that are known. Moreover, it seems likely that if such a theory does ever come into being, it will be far from simple.

When we are faced with a scientific problem of this complexity, experience has shown that it is often more useful to concentrate instead on developing **models**. A scientific model is something like a theory in that it should be able to explain observed phenomena and to make useful predictions. But whereas a theory can be discredited by a single contradictory case, a model can be useful even if it does not encompass all instances of the phenomena it attempts to explain. We do not even require that a model be a credible representation of reality; all we ask is that be able to explain the behavior of those cases to which it is applicable in terms that are consistent with the model itself. An example of a model that you may already know about is the kinetic molecular theory of gases. Despite its name, this is really a model (at least at the level that beginning students use it) because it does not even try to explain the observed behavior of real gases. Nevertheless, it serves as a tool for developing our understanding of gases, and as a starting point for more elaborate treatments.Given the extraordinary variety of ways in which atoms combine into aggregates, it should come as no surprise that a number of useful bonding models have been developed. Most of them apply only to certain classes of compounds, or attempt to explain only a restricted range of phenomena. In this section we will provide brief descriptions of some of the bonding models; the more important of these will be treated in much more detail in later parts of this chapter.

Ionic Bonding

Ever since the discovery early in the 19th century that solutions of salts and other electrolytes conduct electric current, there has been general agreement that the forces that hold atoms together must be electrical in nature. Electrolytic solutions contain ions having opposite electrical charges, opposite charges attract, so perhaps the substances from which these ions come consist of positive and negatively charged atoms held together by electrostatic attraction.

It turns out that this is not true generally, but a model built on this assumption does a fairly good job of explaining a rather small but important class of compounds that are called ionic solids. The most well known example of such a compound is sodium chloride, which consists of two interpenetrating lattices of Na^+ and $Cl^–$ ions arranged in such as way that every ion of one type is surrounded (in three dimensional space) by six ions of opposite charge. The main limitation of this model is that it applies really well only to the small class of solids composed of Group 1 and 2 elements with highly electronegative elements such as the halogens.

According to the ionic electrostatic model, solids such as NaCl consist of positive and negative ions arranged in a crystal lattice. Each ion is attracted to neighboring ions of opposite charge, and is repelled by ions of like charge; this combination of attractions and repulsions, acting in all directions, causes the ion to be tightly fixed in its own location in the crystal lattice.

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form ionic networks (or lattices). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

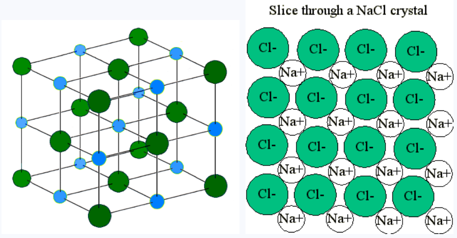
Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

Example 1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

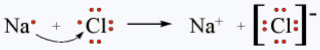
$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)} \tag{1}$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using ***electron-dot symbols*** (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell.

Covalent Bonding

Formation of an ionic bond by complete transfer of an electron from one atom to another is possible only for a fairly restricted set of elements. Covalent bonding, in which neither atom loses complete control over its valence electrons, is much more common. In a **covalent bond** the electrons occupy a region of space *between* the two nuclei and are said to be *shared* by them. This model originated with the theory developed by G.N. Lewis in 1916, and it remains the most widely-used model of chemical bonding. The essential element s of this model can best be understood by examining the simplest possible molecule. This is the **hydrogen molecule ion** H_2^+, which consists of two nuclei and one electron. First, however, think what would happen if we tried to make the even simpler molecule H_2^{2+}. Since this would consist only of two protons whose electrostatic charges would repel each other at all distances, it is clear that such a molecule cannot exist; something more than two nuclei are required for bonding to occur.

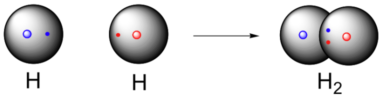
In the hydrogen molecule ion H_2^+ we have a third particle, an electron. The effect of this electron will depend on its location with respect to the two nuclei. If the electron is in the space between the two nuclei, it will attract both protons toward itself, and thus toward each other. If the total attraction energy exceeds the internuclear repulsion, there will be a net bonding effect and the molecule will be stable. If, on the other hand, the electron is off to one side, it will attract both nuclei, but it will attract the closer one much more strongly, owing to the inverse-square nature of Coulomb's law. As a consequence, the electron will now help the electrostatic repulsion to push the two nuclei apart.

We see, then, that the electron is an essential component of a chemical bond, but that it must be in the right place: between the two nuclei. Coulomb's law can be used to calculate the forces experienced by the two nuclei for various positions of the electron, but we have been vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the ‘sharing’ of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in more complex molecules, however, we will need to introduce the concept of **hybrid orbitals**.

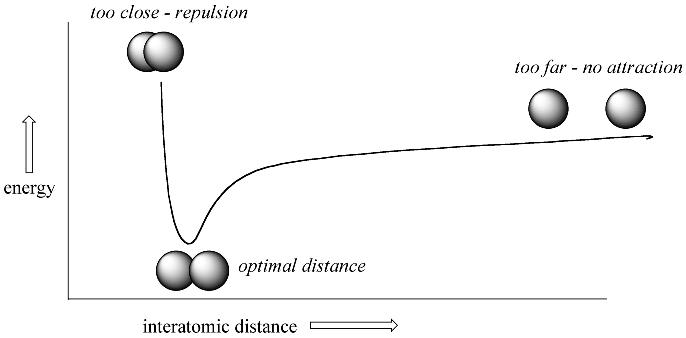
Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.

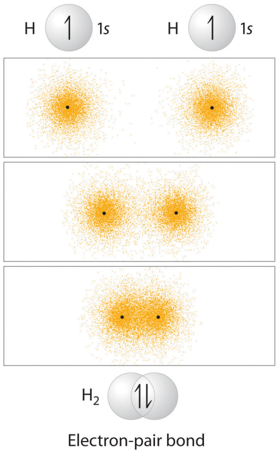


At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74×10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole.

Orbital Overlap: A Second Look

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm. According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond*. When the orbitals of two atoms overlap along the line between the two atomic nuclei (the internuclear axis), the bond is designated as a sigma (σ) bond. The formation of a sigma bond between two H atoms is shown here:



Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H–H Bond in H_2. *The formation of* H_2 *from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an* H_2 *molecule increases the electron density in the region between the two positively charged nuclei.*

All orbitals other than *s* orbitals are able to form a second type of covalent bond, based on their ability to overlap, simultaneously, both above and below the internuclear axis of the two bonding atoms. This type of overlap is called a pi (pi) bond.

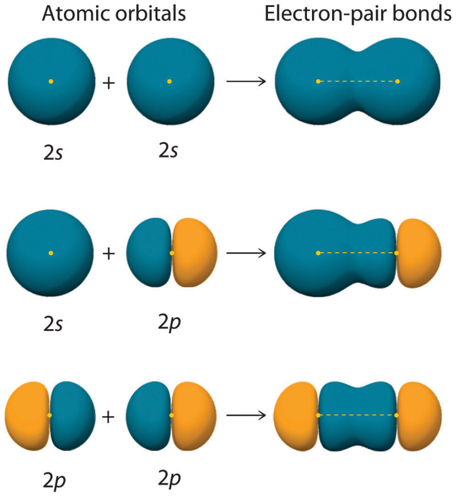
There are two basic assumptions for covalent bonding theory:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond. Sigma bonds are generally stronger than pi bonds because the overlap is greater in sigma bonds than in pi bonds.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms. (Described later when we discuss hybrid orbitals.)

Sigma Bond Overlapping

The figure below shows a sigma bond formed by the overlap of two *s* atomic orbitals, two *p* atomic orbitals, and an *s* and an *p* orbital. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

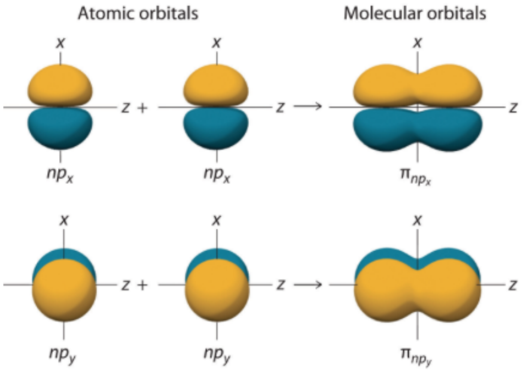


Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two s atomic orbitals (a), an s and an p atomic orbital (b), and two p atomic orbitals (c).

Pi Bond Overlapping

The figure below shows a pi bond formed by the overlap of two *p* atomic orbitals, and a p and a d orbital. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "parallel" with each other).

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in the figure below. In a π bond, the regions of orbital overlap lie above and below the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.



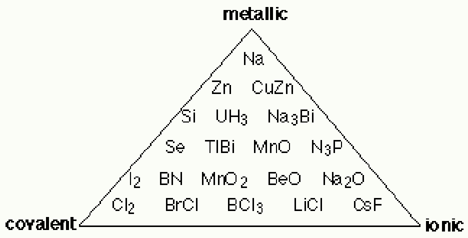
Formation of π Molecular Orbitals from np_x *and* np_y *Atomic Orbitals on Adjacent Atoms.*

Metallic Bonding

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). **Metallic bonding** is sort of like covalent bonding, because it involves sharing electrons. The simplest model of metallic bonding is the "sea of electrons" model, which imagines that the atoms sit in a sea of valence electrons that are delocalized over all the atoms. Because there are not specific bonds between individual atoms, metals are more flexible. The atoms can move around and the electron sea will keep holding them together. Some metals are very hard and have very high melting points, while others are soft and have low melting points. This depends roughly on the number of valence electrons that form the sea.

A False Dichotomy: The Ionic vs. Colvalent

The covalent-ionic continuum described above is certainly an improvement over the old covalent -*versus* - ionic dichotomy that existed only in the textbook and classroom, but it is still only a one-dimensional view of a multidimensional world, and thus a view that hides more than it reveals. The main thing missing is any allowance for the type of bonding that occurs between more pairs of elements than any other: metallic bonding. Intermetallic compounds are rarely even mentioned in introductory courses, but since most of the elements are metals, there are a lot of them, and many play an important role in metallurgy. In metallic bonding, the valence electrons lose their association with individual atoms; they form what amounts to a mobile "electron fluid" that fills the space between the crystal lattice positions occupied by the atoms, (now essentially positive ions.) The more readily this electron delocalization occurs, the more "metallic" the element.



Thus instead of the one-dimension chart shown above, we can construct a triangular diagram whose corners represent the three extremes of "pure" covalent, ionic, and metallic bonding.

Summary

The covalent bond is formed when two atoms are able to share electrons:

$$A\cdot \;+\; B\cdot \;\rightarrow\; A:B$$

whereas the ionic bond is formed when the "sharing" is so unequal that an electron from atom A is completely lost to atom B, resulting in a pair of ions:

$$A\cdot \;+\; B\cdot \;\rightarrow\; A^{+}\;:B^{-}$$

The two extremes of electron sharing represented by the covalent and ionic models appear to be generally consistent with the observed properties of molecular and ionic solids and liquids. But does this mean that there are really two kinds of chemical bonds, ionic and covalent?

Contributors

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Modified by Tom Neils (Grand Rapids Community College)

3.4 Ionic Compounds: Formulas and Names

Skills to Develop

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

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

Ionic Compounds

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

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 $3.4 Ionic Compounds. 2$

Table $3.4IonicCompounds.1$: *Names of Some Ionic Compounds*

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

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an –*ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table $3.4 Ionic Compounds. 2$

Table $3.4IonicCompounds.2$: *Names of Some Polyatomic Ionic Compounds*

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

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table. 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.

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

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see [link]), 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 $3.4 IonicCompounds.3$

Table $3.4 IonicCompounds.3$: *Names of Some Transition Metal Ionic Compounds*

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

Out-of-date nomenclature used the suffixes –*ic* and –*ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example $3.4 IonicCompounds.1$: Naming Ionic Compounds

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

a. Fe_2S_3
b. CuSe
c. GaN

d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^{-}, and SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{4+}, and Ti^{3+}. These charges are used in the names of the metal ions:

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

Exercise $3.4 IonicCompounds.1$

Write the formulas of the following ionic compounds:

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

Answer:

(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) CrF_6

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized.

Contributors

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

3.5 Covalently-Bonded Species: Formulas and Names

Skills to Develop

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

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

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table $3.5 Covalently-Bonded Species.3$.

Table $3.5 Covalently-Bonded Species.3$: *Nomenclature Prefixes*

Number	Prefix	Number	Prefix
1 (sometimes omitted)	mono-	6	hexa-
2	di-	7	hepta-
3	tri-	8	octa-

Number	Prefix	Number	Prefix
4	tetra-	9	nona-
5	penta-	10	deca-

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table $3.5 Covalently - Bonded Species.4$.

Table $\mathbf{3.5 Covalently - Bonded Species.4}$**:** *Names of Some Molecular Compounds Composed of Two Elements*

Compound	Name	Compound	Name
SO_2	sulfur dioxide	BCl_3	boron trichloride

Compound	Name
SO_3	sulfur trioxide
NO_2	nitrogen dioxide

Compound	Name
SF_6	sulfur hexafluoride
PF_5	phosphorus pentafluoride

Compound	Name	Compound	Name
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. You should commit to memory the common names of compounds as you encounter them.

Example 3.5$Covalently - BondedSpecies.2$: 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 $3.5 Covalently-Bonded Species.2$

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

Binary Compounds of Hydrogen

Covalently-bonded compounds that consist of only H atoms and one atom of one other element are named as if they are ionically-bonded. Specifically, the number of atoms is not indicated in the name. Thus, HI is named hydrogen iodide, and H_2S is named hydrogen sulfide. Be aware that the systematic name is **not** dihydrogen monoxide.

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 $3.5 Covalently-Bonded Species.5$.

Table $3.5 Covalently-Bonded Species.5$: Names of Some Simple Acids

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

Oxyacids

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

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

For example, consider H_2CO_3 (which you might be tempted to call “hydrogen carbonate”). To name this correctly, “hydrogen” is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table $3.5 Covalently-Bonded Species.6$. 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 $3.5 Covalently-Bonded Species.6$: 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

Summary

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

Contributors

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

3.6 Electronegativity and Bond Polarity

Skills to Develop

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

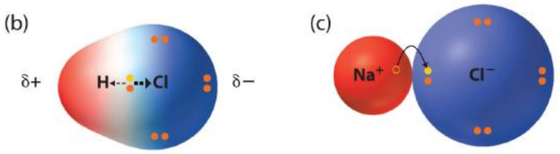
The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, whereas the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the one valence electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally or nearly equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Percent Ionic Character of a Covalent polar Bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure 4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

Nonpolar covalent bond
Bonding electrons shared
equally between two atoms.
No charges on atoms.



Polar covalent bond
Bonding electrons shared
unequally between two atoms.
Partial charges on atoms.

Ionic bond
Complete transfer of one or more
valence electrons.
Full charges on resulting ions.

Figure 4: *The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.*

One method for calculating the percent ionic character of a bond is to use the following equation:

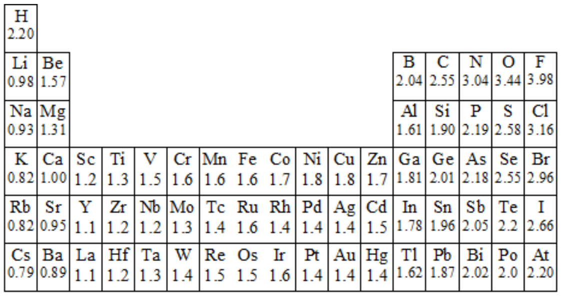
$$\text{\% ionic character} = \frac{EN_{higher} - EN_{lower}}{EN_{higher}} \times 100$$

≥ 50% means the bond is ionic

> 5% but < 50% means the bond is polar covalent

≤ 5% means the bond is pure (non-polar) covalent

Table of Pauling Electronegativities



H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.6	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.1	Zr 1.2	Nb 1.2	Mo 1.3	Tc 1.4	Ru 1.6	Rh 1.4	Pd 1.4	Ag 1.4	Cd 1.5	In 1.78	Sn 1.96	Sb 2.05	Te 2.2	I 2.66
Cs 0.79	Ba 0.89	La 1.1	Hf 1.2	Ta 1.3	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.4	Au 1.4	Hg 1.4	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.20

Example 1

What is the % ionic character of a P-S bond?

Solution

Add text here.

Exercise 1

Add exercises text here.

Answer

Add texts here. Do not delete this text first.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^{+}}{\overset{\text{less electronegative}}{A}} \quad - \quad \underset{\delta^{-}}{\overset{\text{more electronegative}}{B}} \tag{1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^{+}}{H} \quad - \quad \overset{\delta^{-}}{Cl} \tag{2}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges.

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 4).

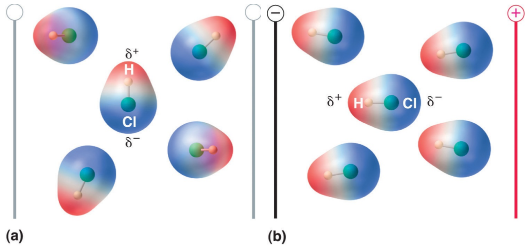


Figure* 5*: *Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.*

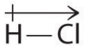
The measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta^+}{H} \quad - \quad \overset{\delta^-}{Cl} \tag{3}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta^+}{H} \quad - \quad \overset{0.18\delta^-}{Cl} \tag{4}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 6 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 6 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 2.

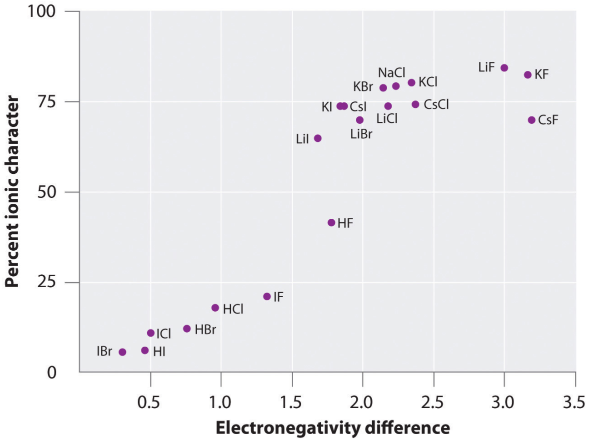


***Figure 6**: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.*

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Modified by Tom Neils (Grand Rapids Community College)

3.7 Lewis Structures

Skills to Develop

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 1):

- The electrons in the two atoms repel each other because they have the same charge ($E > 0$).
- Similarly, the protons in adjacent atoms repel each other ($E > 0$).
- The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.

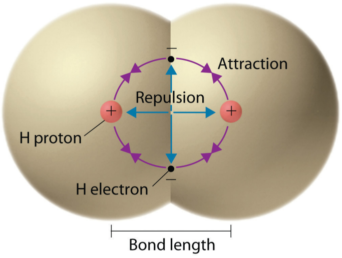


Figure 1: *Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.*

A plot of the potential energy of the system as a function of the internuclear distance (Figure 2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures 1 and 2, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

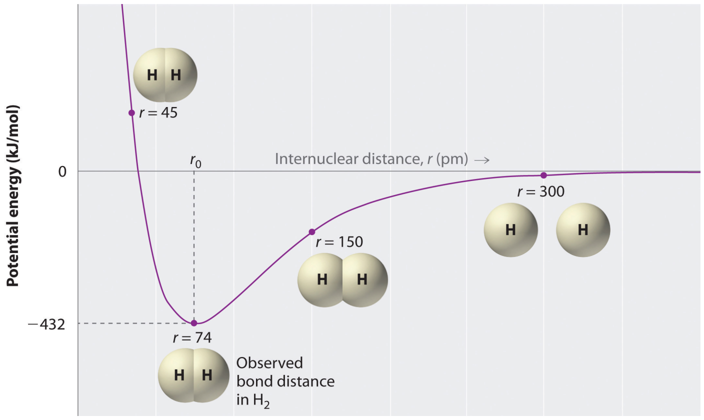


Figure 2: *A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.*

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

Using Lewis Dot Symbols to Describe Covalent Bonding

It is usually easier to figure out a problem if you can draw a picture, either mental or real, of what is happening. This is often done in physics and mathematics, and it is especially helpful when looking at the bonding, structure, physical properties, and reactivity of compounds.

The most common picture, or model, of elements and compounds used is the Lewis Dot Structure. These pictures show you the type(s) of atom(s) involved, their position in the molecule, and where their valence electrons are situated.

To draw structures of substances you need to know:

1. the electronegativities of the elements so that you can decide if the atoms form ionic bonds or covalent bonds.
2. the number of valence electrons so that you can determine what ions will likely form (if the bonding will be ionic) or how many electrons will need to be shared in bonds (if the bonding will be covalent.)

GENERAL TERMS FOR LEWIS DOT STRUCTURES:

1. Dot • one dot represents one valence electron (found on odd-electron particles)
2. Pair of Dots •• a pair of dots represents a nonbonding (lone) pair of electrons that are **not** involved in a covalent bond and "belong to" only one atom
3. Dash each dash represents two electrons that are shared between two atoms as a covalent bond.

One dash — a single bond; one set of two electrons shared; also a sigma (σ) bond

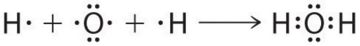
Two dashes = a double bond; two sets of two electrons shared; one sigma (σ) and one pi (π) bond

Three dashes ≡ a triple bond: three sets of two electrons shared; one sigma and two pi (π) bonds

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:

Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:

In CHM 120, you should always use lines to represent bonds. The use of dots will be reserved for non-bonding (lone) electron pairs.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

Skills to Develop

THE EASY METHOD PROCEDURE TO DETERMINE A LEWIS DOT STRUCTURE

In this process, the basic concept of this method is that all valence electrons present will be taken away from the individual atoms and pooled together. They will first be doled out to form the requisite number of bonds. The remaining valence electrons will then be added to individual atoms as lone pairs to complete the octet of each atom.

1. Calculate the total number of valence electrons required for each atom to have an octet, or eight valence electrons. The major exception to this rule is that hydrogen wants only two (2) valence electrons. The other two most commonly-occurring exceptions are Be (4) and B (6) valence electrons.

Thus, the process for step one is 2 x (# of H atoms) + 8 x (# of most other atoms) = valence electrons needed

2. Calculate the total number of valence electrons in the given species.

If you have a **polyatomic anion**, you must add the number of '-' charges because there are extra valence electrons.

If you have a **polyatomic cation**, you must subtract the number of '+' charges because there are missing valence electrons.

3. Subtract result **2** from result **1**. This is the number of valence electrons lacking for each atom to have its own octet. This number of electrons will have to be shared in bonds.

4. Divide result **3** by two, because there are two electrons per bond. This is the number of covalent bonds you must use!

5. Connect the atoms in the formula together with the number of bonds from result **4**. Helpful hints:

i) H atoms form only one bond.

ii) The first atom in the formula is usually the central atom to which the other atoms bond

iii) If the particle has only three atoms, and each atom is of a different element, the atom in the middle of the formula is usually in the middle of the structure.

iv) species are as symmetrical as possible when there are several central atoms

v) For **neutral** species:

Group IV atoms usually form four bonds

Group V atoms usually form three bonds

Group VI atoms usually form two bonds

Group VII atoms usually form one bond

6. Add in electrons as **non-bonding pairs** or **lone pairs (groups of two)**, so that each atom has eight electrons around it.

7. Count the total number of electrons in the structure. The number should be equal to the number of electrons in result **2**.

CAUTIONS:

1. Never put a lone pair on an H atom.

2. The only common substances that have a lone pair on a C atom are CO and CN^-. Other than those two particles, you should not put a lone pair on a C atom.

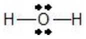
Now let’s apply this procedure to some particular compounds, beginning with one we have already discussed.

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. (1 O atom) x (8) + (2 H atoms) x (2) = 12 valence electrons needed
2. (1 O atom) x (6) + (2 H atoms) x (1) = 8 valence electrons present.
3. 12-8 = 4 electrons short, thus 4 electrons must be shared
4. 4 shared electrons/ 2 electrons per bond = 2 bonds
5. Connect the each of the two H atoms to the O atom with one single bond each.

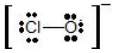
6. Add the remaining 4 electrons to the oxygen (as two lone pairs) to give the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^{-} Ion

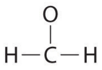
1. (1 O atom) x (8) + (1 Cl atom) x (8) = 16 valence electrons needed
2. (1 O atom) x (6) + (1 Cl atom) x (7) + 1 = 14 valence electrons present.
3. 16 - 14 = 2 electrons short, thus 2 electrons must be shared
4. 2 shared electrons/ 2 electrons per bond = 1 bond
5. Connect the two atoms with one single bond .
6. Add the remaining 12 electrons as lone pairs, with 3 pairs on the O atom and 3 pairs on the Cl atom, giving the following structure:



Each atom now has an octet of electrons. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^{-} is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

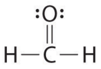
The CH_2O Molecule

1. (1 O atom) x (8) + (1 C atom) x (8) + (2 H atoms) x (2) = 20 valence electrons needed
2. (1 O atom) x (6) + (1 C atom) x (4) + (2 H atoms) x (1) = 12 valence electrons present.
3. 20 - 12 = 8 electrons short, thus 8 electrons must be shared
4. 8 shared electrons/ 2 electrons per bond = 4 bonds
5. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. Connect the two H atoms and the O atom to the C atom with with one single bond each, giving the structure:



6. There is still one more bond that you must use in the structure. At this point, the C atom has only three bonds and the O atom has only one bond. Thus, putting one more bond between the C and the O, creating a double bond, will satisfy all bonding requirements.

7. Add the remaining 4 electrons as two lone pairs on the O atom, giving the following structure:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

Asked for: Lewis electron structures

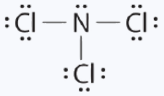
Strategy:

Use the six-step procedure to write the Lewis electron structure for each species.

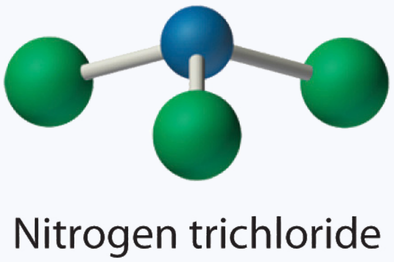
Solution:

a. NCl_3 Determine number of bonds needed

1. (1 N atom) x (8) + (3 Cl atoms) x (8) = 32 valence electrons needed
2. (1 N atom) x (5) + (3 Cl atoms) x (7) = 26 valence electrons present.
3. 32 - 26 = 6 electrons short, thus 6 electrons must be shared
4. 6 shared electrons/ 2 electrons per bond = 3 bonds
5. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. Connect the three Cl atoms with the central N atom with three single bonds.
6. You have used 6 electrons. Add the remaining 20 electrons on to the structure as lone pairs, to ensure that each atom has an octet (1 lone pair for N, and 3 lone pairs for each Cl.)



Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



b. S_2^{2-} ion Determine number of bonds needed

1. (2 S atoms) x (8) = 16 valence electrons needed

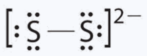
2. (2 S atoms) x (6) + 2 = 14 valence electrons present.

3. 16-14 = 2 electrons short, thus 2 electrons must be shared

4. 2 shared electrons/ 2 electrons per bond = 1 bond

5. Connect the each of the two S atoms with one single bond each.

6. You have used two electrons. Add the remaining 12 electrons to the S atoms (as three lone pairs per S atom) to give the following structure:



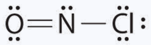
c. NOCl Determine number of bonds needed

1. (1 N atom) x (8) + (1 O atom) x (8) + (1 Cl atom) x (8) = 24 valence electrons needed
2. (1 N atom) x (5) + (1 O atom) x (6) + (1 Cl atom) x (7)= 18 valence electrons present.
3. 24-18 = 6 electrons short, thus 6 electrons must be shared
4. 6 shared electrons/ 2 electrons per bond = 3 bonds
5. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. Also, this molecule falls into the category of a particle that has only three atoms, and each atom is of a different element, so the atom in the middle of the formula is usually in the middle of the structure. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:

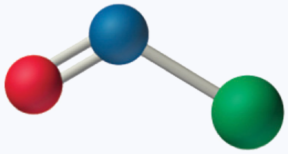
O—N—Cl

6. There is still one more bond that you must use in the structure. At this point, the N atom has only two bonds and the O atom has only one bond. Thus, putting one more bond between the N and the O, creating a double bond, will satisfy all bonding requirements. The Cl, as a halogen, is stable with just one bond.

7. You have used 6 electrons. Add the remaining 12 electrons as two lone pairs on the O atom, one lone pair on the N atom, and three lone pairs ion the Cl atom giving the following structure:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



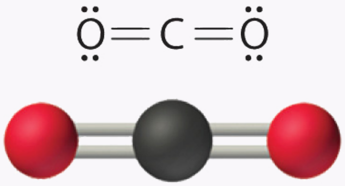
Nitrosyl chloride

Exercise 1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

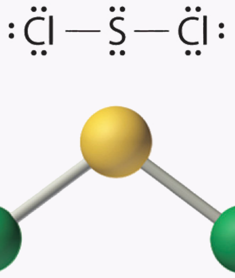
Answer:

1.



Carbon dioxide

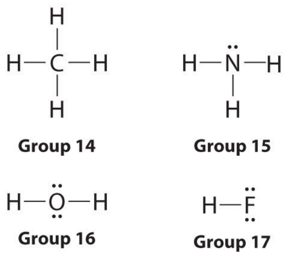
2.



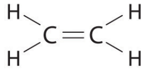
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group VIIA (the halogens), this number is one; for the elements of Group VIA (the chalcogens), it is two; for Group VA elements, three; and for Group IVA elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Lewis structures explain why the elements of groups IVA–VIIA form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. Diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

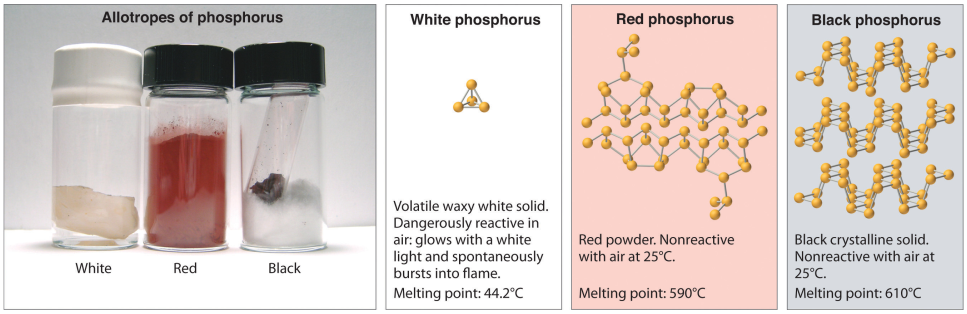


***Figure* 3**: *The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains* P_4 *tetrahedra, red phosphorus is a network of linked* P_8 *and* P_9 *units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge assigned to the atoms. A formal charge is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

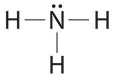
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$formal\ charge = \underset{(free\ atom)}{valence\ e^-} - \underset{(atom\ in\ Lewis\ structure)}{\left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)} \quad \text{(atom in Lewis structure)}$$

To illustrate this method, let’s calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group VA). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0 \tag{1}$$

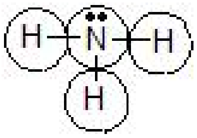
A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0 \tag{2}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

A second way to assign electrons is to draw the Lewis dot structure and then draw a circle around each atom in the structure. The circle should be drawn so that every bond is cut in half, and so that lone pairs on an atom are included in the circle. The electrons in the circle around the atom are the electrons that are assigned to that atom:



The formal charge is calculated by subtracting the number of assigned electrons (in the circle) from the number of valence electrons.

Typically, the structure with the most zero formal charges on the atoms is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

Example 2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

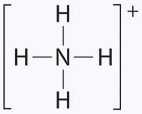
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



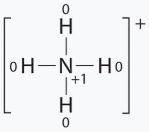
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0 \tag{3}$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0 \tag{4}$$

The formal charges on the atoms in the NH_4^+ ion are thus

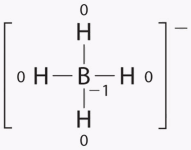


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 2

Write the formal charges on all atoms in BH_4^-.

Answer:



If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

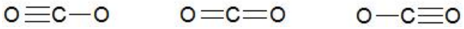
Using Formal Charges to Distinguish Viable Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

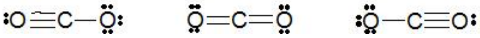
CO_2

1. (1 C atom) x (8) + (2 O atoms) x (8)= 24 valence electrons needed
2. (1 C atom) x (4) + (2 O atoms) x (6) = 16 valence electrons present.
3. 24 - 16 = 8 electrons short, thus 8 electrons must be shared
4. 8 shared electrons/ 2 electrons per bond = 4 bonds

5. Carbon is less electronegative than oxygen, so carbon is the central atom. Connect the two O atoms with the central C atom with one single bond each. You have two more bonds that need to be added to the structure. These two bonds could be added in three different ways:



6. You have used 8 electrons. Add the remaining 8 electrons on to the O atoms as lone pairs to ensure that each atom has an octet:



All three Lewis structures give all three atoms an octet. How do we decide between these three possibilities? First, recognize that the left form and the right form are equivalent; that is they each have one singly-bonded O atom and one triply-bonded O atom. The middle structure is not equivalent to either of the side structures. The formal charges for the two non-equivalent Lewis structures of CO_2 are as follows:

Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

The Lewis structure with the set of formal charges closest to zero is usually (but not always) the most stable.

Example 3: The Thiocyanate Ion

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

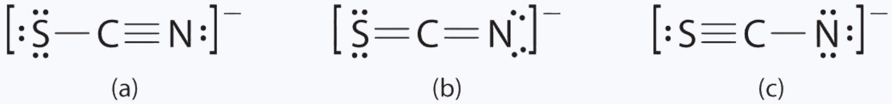
Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

A. Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.
B. Calculate the formal charge on each atom.
C. Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



(a) (b) (c)

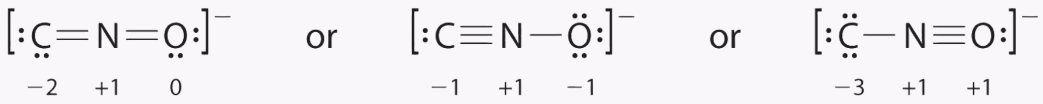
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6-\left(6+\frac{2}{2}\right)=-1.5-\left(4+\frac{4}{2}\right)=-1$ In (c), nitrogen has a formal charge of −2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, −1 versus +1, −2.

Exercise 1: The Fulminate Ion

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer:



The second structure is predicted to be more stable.

Summary

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group IVA elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group VA elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one.

Contributors

- Modified by Joshua Halpern (Howard University)
- Modified by Tom Neils (Grand Rapids Community College)

3.8 Resonance and Formal Charge Revisited

Skills to Develop

- To understand the concept of resonance.

Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding a single polyatomic species including fractional bonds and fractional charges. Resonance structure are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integer number of covalent bonds. When drawing resonance structures, you are allowed to move only lone pairs of electrons and pi bonds. You cannot move any atoms, and you cannot make any new sigma bonds or remove any existing sigma bonds.

Sometimes one Lewis Structure is not Enough

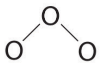
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

Ozone (O_3)

First we calculate the number of bonds needed

1. (3 O atoms) x (8) = 24 valence electrons needed
2. (3 O atoms) x (6) = 18 valence electrons present.
3. 24 - 18 = 6 electrons short, thus 6 electrons must be shared
4. 6 shared electrons/ 2 electrons per bond = 3 bonds
5. Connect the three atoms with one single bond. A three-membered ring is not impossible, but not very likely.

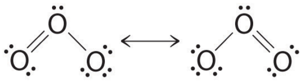
   We know that ozone has a V-shaped structure from the information given above, so one O atom is central:

6. There is still one more bond to add. You could place that bond on either side, and then add the remaining 12 electrons as lone pairs, with 3 pairs on the singly-bonded O atom, 2 pairs on the doubly-bonded O atom, and one pair on the central O atom giving the following structures:

Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

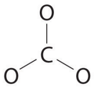
> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The Carbonate (CO_3^{2-}) Ion

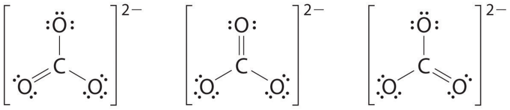
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

First we calculate the number of bonds needed

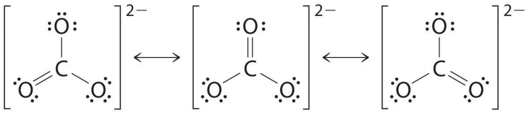
1. (3 O atoms) x (8) + (1 C atom) x (8) = 32 valence electrons needed
2. (3 O atoms) x (6) + (1 C atom) x (4) + 2 = 24 valence electrons present.
3. 32 - 24 = 8 electrons short, thus 8 electrons must be shared
4. 8 shared electrons/ 2 electrons per bond = 4 bonds
5. The C atom is the least electronegative element, so it is in the center. Connect the three O atoms to the C atom with one single bond per O atom.



6. There is still one more bond to add. You can place that bond as a pi bond to any one of the O atoms, and then add the remaining 16 electrons as lone pairs, with 3 pairs on the singly-bonded O atoms, and 2 pairs on the doubly-bonded O atom, giving the following three structures:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

Example 1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

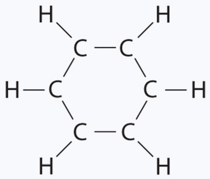
Strategy:

A. Calculate the number of bonds needed for the molecule
B. Draw the resonance structures for benzene.

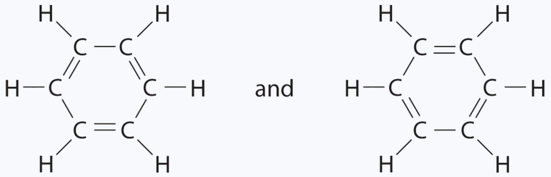
Solution:

1. (6 C atoms) x (8) + (6 H atoms) x (2) = 60 valence electrons needed
2. (6 C atoms) x (4) + (6 H atoms) x (1) = 30 valence electrons present.
3. 60 - 30 = 30 electrons short, thus 30 electrons must be shared
4. 30 shared electrons/ 2 electrons per bond = 15 bonds

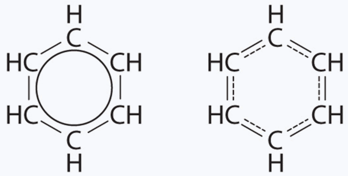
5. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



This structure has 12 bonds, so there are still 3 bonds to add. The only option is to place a pi bond between every other C atom. But there are 2 ways to do this**:**



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

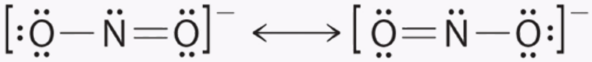


Benzene

Exercise 1: Nitrate Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 1. Once would expect the double bonds to be shorter than the single bonds, but if once overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is mechanism that allows us to use all of possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

Modified by Tom Neils (Grand Rapids Community College)

3.9 Exceptions to the Octet Rule

Skills to Develop

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be nitrogen monoxide also called nitric oxide (NO.

1. (1 O atom) x (8) + (1 N atom) x (8) = 16 valence electrons needed
2. (1 O atom) x (6) + (1 N atom) x (5) = 11 valence electrons present.
3. 16 - 11 = 5 electrons short, thus 5 electrons must be shared
4. 5 shared electrons/ 2 electrons per bond = 2.5 bonds How can you have a half of a bond? You can't according to Lewis dot structure rules. Instead, draw a structure with two bonds (essentially ignoring the 1/2 bond).
5. The two bonds have to be placed between the N and O atoms.

N=O

6. You have used up 4 of the 11 electrons. Add in the remaining seven as 3 lone pairs and one unpaired electron. But where should the lone pairs and the one unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. Oxygen normally has six valence electrons. If we give the O atom two lone pairs of electrons, and it participates in two bonds (a double bond) with nitrogen, the O atom will have a formal charge of 0. Nitrogen normally has five valence electrons. If the N atom participates in two bonds with oxygen and is assigned one lone pair along with one single electron, the formal charge on the N atom will be 0. The O atom will have an octet of valence electrons, but the N atom will have only seven valence electrons. That is acceptable because this molecule is an odd-elctron particle and one atom in the molecule must have fewer than eight valence electrons.

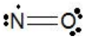


***Figure** : The proper Lewis structure for NO molecule*

Free Radicals

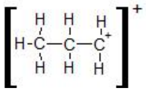
There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species, which we call **free radicals**, are highly reactive. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$.

Exception 2: Incomplete Octets - Carbocations

The second exception to the octet rule is when there are too few valence electrons on one atom, which results in an incomplete octet. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. But they are also found in organic chemistry as reaction intermediates - species that are formed in one step of a reaction, but then used up in some following step. Let's take a look at one such carbocation, $CH_3CH_2CH_2^+$:

1. (3 C atoms) x (8) + (7 H atoms) x (2) = 38 valence electrons needed

2. (3 C atoms) x (4) + (7 H atoms) x (1) -1 = 18 valence electrons present.
3. 38 - 18 = 20 electrons short, thus 20 electrons must be shared
4. 20 shared electrons/ 2 electrons per bond = 10 bonds But, how can you have 10 bonds if you have only 18 electrons present? You can't . Instead, draw a structure with 9 bonds (subtract one bond from the number of bonds that you calculated.)
5. You can draw single bonds between the C and H atoms, using up all 18 electrons, as shown here:



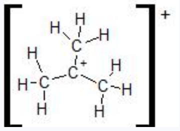
The problem with this structure is that C atom on the right has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with carbon. A carbocation such as this is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Example 1: NF_3

Draw the Lewis structure for $(CH_3)_3C^+$

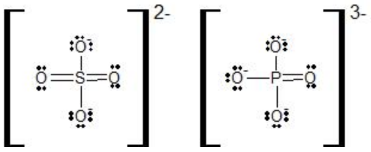
SOLUTION

1. (4 C atoms) x (8) + (9 H atoms) x (2) = 50 valence electrons needed
2. (4 C atoms) x (4) + (9 H atoms) x (1) -1 = 24 valence electrons present.
3. 50 - 24 = 26 electrons short, thus 26 electrons must be shared
4. 26 shared electrons/ 2 electrons per bond = 13 bonds But, how can you have 13 bonds if you have only 24 electrons present? You can't . Instead, draw a structure with 12 bonds (subtract one bond from the number of bonds that you calculated.)
5. You can draw single bonds between the C and H atoms, using up all 24 electrons, as shown here:



Exception 3: Expanded Valence Shells

Compounds containing expanded valence shell atoms occur when the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten, twelve, or even fourteen valence electrons. Particles with expanded octets involve a nonmetal central atom from the third row or below, and a highly electronegative terminal atom. We will not work with any of these particles, but it is important to note that two common polyatomic ions, SO_4^{2-} and PO_4^{3-}, can be drawn, in their most stable resonance form, with the S and P atoms as expanded valence shell atoms:



Summary

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

References

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.

2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

Contributors

- Mike Blaber (Florida State University)
- Modified by Tom Neils (Grand Rapids Community College)

3.10 Shapes of Molecules - VSEPR Theory and Valence Bond Theory

VSEPR Theory

Valence **S**hell **E**lectron **P**air **R**epulsion Theory uses the basic idea that electron pairs are mutually repulsed to predict the arrangement of electron pairs around a central atom (an atom that has at least two other atoms bonded directly to it). The key to correctly applying VSEPR Theory is to start with a correct Lewis dot structure. From a correct Lewis dot structure, it is a straightforward process to determine the shape of a molecule or polyatomic ion by determining the arrangement of electron pairs around every central atom in the molecule or polyatomic ion.

The step-by-step process to determine the shape around each central atom is

1. Draw the Lewis dot structure.

2. Apply the following analysis to each separate, central atom (where a central atom is an atom with two or more other atoms bonded directly to it.)

a) Find the number of "things attached" to the central atom, where a "thing attached" is either an atom or a non-bonding electron pair.

(Actually, you are counting the number of hybrid orbitals on the central atom, but that is the next theory to be discussed.)

It is important to remember that you are **not** counting bonds!

b) Find the **Electron Group Arrangement (EGA)** in the table below

# of Things Attached	Electron Group Arrangement	Ideal Bond Angle	Hybridization of Central Atom
2	line (linear shape)	180	sp
3	trigonal plane(trigonal planar shape)	120	sp^2
4	tetrahedron (tetrahedral shape)	109.5	sp^3

c) Find the **Molecular Geometry (MG)** of the particle, determined by counting up the number of atoms and the number of lone pairs and using this table:

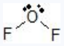
Hybridization of Central Atom (see Valence Bond Theory)	# of atoms attached	# of lone pairs attached	[illegible]
sp hybridized central atom:			

	2	line	CO_2	180
sp^2 hybridized central atom:				
	3	trigonal plane	BF_3	120
	2	bent	SO_2	<120
sp^3 hybridized central atom:				
	4	tetrahedron	CH_4	109.5
	3	trigonal pyramid	NH_3	<109.5
	2	bent	H_2O	<109.5

Example 1

Determine the Electron Group Arrangement and Molecular Geometry about the central atom(s) in a) OF_2 and b) CH_3CN.

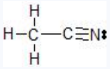
Solution

a) The Lewis dot structure of OF_2 is  (leaving off the lone pairs on the non-central F atoms.)

There are 2 atoms and 2 lone pairs attached to the central O atom, for a total of 4 "things attached."

From the two tables above, we can see that the O atom must have an EGA of a tetrahedron, and its MG is bent.

b) The Lewis dot structure of CH_3CN is



There are 4 atoms and 0 lone pairs attached to the central C atom on the left, for a total of 4 "things attached."

From the two tables above, we can see that this C atom must have an EGA of a tetrahedron, and its MG is also a tetrahedron.

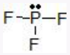
There are 2 atoms and 0 lone pairs attached to the central C atom on the right, for a total of 2 "things attached."

From the two tables above, we can see that this C atom must have an EGA of a line, and its MG is also a line.

Exercise 1

Determine the Electron Group Arrangement and Molecular Geometry about the central atom(s) in a) PF_3 and b) CH_2NH.

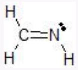
Answer

a) The Lewis dot structure of PF_3 is  (leaving off the lone pairs on the non-central F atoms.)

There are 3 atoms and 1 lone pair attached to the central P atom, for a total of 4 "things attached."

From the two tables above, we can see that the P atom must have an EGA of a tetrahedron, and its MG is a trigonal pyramid.

b)The Lewis dot structure of CH_2NH is



There are 3 atoms and 0 lone pairs attached to the central C atom on the left, for a total of 3 "things attached."

From the two tables above, we can see that this C atom must have an EGA of a trigonal plane, and its MG is also a trigonal plane.

There are 2 atoms and 1 lone pair attached to the central N atom on the right, for a total of 3 "things attached."

From the two tables above, we can see that this N atom must have an EGA of a trigonal plane, and its MG is bent.

Valence Bond Theory

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds to create the common electron group arrangements. These new orbital combinations are called **hybrid atomic orbitals** because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridizing One s Orbital and Three p Orbitals

Carbon atoms typically form four covalent bonds, and have electron group arrangement of a tetrahedron because there are four "things attached" to the central C atom. We can explain the tetrahedral shape by proposing that the 2*s* orbital and the three 2*p* orbitals on a carbon atom mix together to give a set of four degenerate sp^3 (“s-p-three”) hybrid orbitals, each containing a single electron.

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 1). Like all the hybridized orbitals discussed earlier, the *sp^3* hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

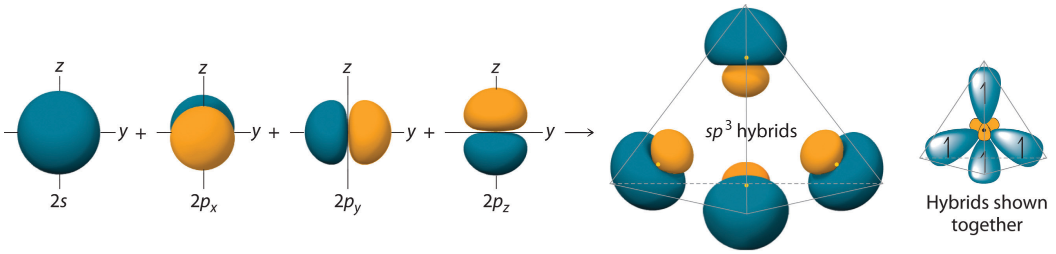
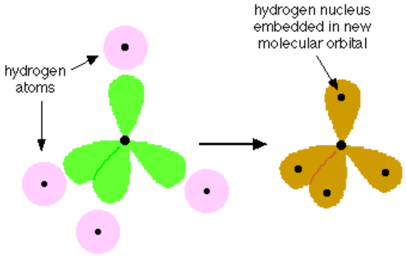


Figure* 1*: *Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.*

An sp^3 hybrid orbital looks a bit like half of a p orbital, and the four sp^3 hybrid orbitals arrange themselves in space so that they are as far apart as possible. You can picture the nucleus as being at the centre of a tetrahedron (a triangularly based pyramid) with the orbitals pointing to the corners. For clarity, the nucleus is drawn far larger than it really is.

What happens when the bonds are formed?

Remember that hydrogen's electron is in a 1s orbital - a spherically symmetric region of space surrounding the nucleus where there is some fixed chance (say 95%) of finding the electron. When a covalent bond is formed, the atomic orbitals (the orbitals in the individual atoms) merge to produce a new molecular orbital which contains the electron pair which creates the bond.

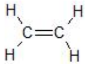


Four molecular orbitals are formed, looking rather like the original sp^3 hybrids, but with a hydrogen nucleus embedded in each lobe.

Hybrid orbital theory can be applied to molecules of ammonia (NH_3) , which has three atoms and one lone pair attached to the central N atom. This means that the N atom is sp^3 hybridized. Three *sp^3* orbitals form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an *sp^3* hybridized oxygen atom that uses two *sp^3* orbitals to bond to two H atoms, and two orbitals to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O.

Hybridizing One s Orbital and Two p Orbitals

Ethene, C_2H_4, is a molecule in which all of the atoms lie in a plane, with 120º bond angles between all of the atoms:



To explain this structure, we can generate three equivalent hybrid orbitals on each C atom by combining the 2*s* orbital of the carbon and two of the three degenerate 2*p* orbitals. This mixing results in each C atom possessing a set of three equivalent hybrid orbitals with one electron each. The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure 2). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, carbon is said to be sp^2 *hybridized* (pronounced “s-p-two” or “s-p-squared”).

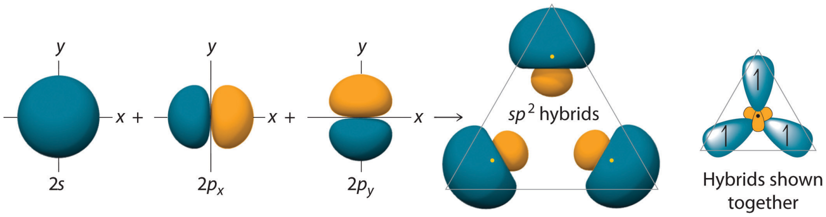
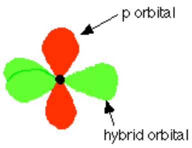


Figure 2: *Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.*

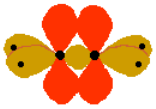
Two of the sp^2 hybrid atomic orbitals on each C atom can can overlap with the s orbitals on two H atoms. The third hybrid orbital on each C atom can overlap to form a sigma bond between the two C atoms. Both C atoms have one 2p orbital that has yet to be used for bonding. When the C atoms form a sigma bond and are pulled close together, a pi bond can also form between the two C atoms because the p-orbitals can overlap above and below the internuclear axis. The result to form a trigonal planar structure.

The entire bonding process looks like this (with the sp^2 hybrid orbitals in bright green and the unhybridized p orbitals in red):

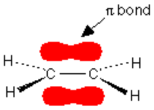


The two carbon atoms and four hydrogen atoms would look like this before they joined together:

The various atomic orbitals which are pointing towards each other now merge to give molecular orbitals, each containing a bonding pair of electrons. These are ***sigma bonds*** - just like those formed by end-to-end overlap of atomic orbitals in, say, ethane.



The p orbitals on each carbon are not pointing towards each other, and so we'll leave those for a moment. In the diagram, the black dots represent the nuclei of the atoms. Notice that the p orbitals are so close that they are overlapping sideways.



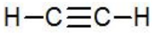
This sideways overlap also creates a π *bond.*

For clarity, the sigma bonds are shown using lines - each line representing one pair of shared electrons. The various sorts of line show the directions the bonds point in. An ordinary line represents a bond in the plane of the screen (or the paper if you've printed it), a broken line is a bond going back away from you, and a wedge shows a bond coming out towards you.

Be clear about what a π bond is. It is a region of space in which you can find the two electrons which make up the bond. Those two electrons can live anywhere within that space. It would be quite misleading to think of one living in the top and the other in the bottom.

Hybridizing One s Orbital and One p Orbital

Ethyne, C_2H_2, is a molecule in which all of the atoms lie in a straight line:



To explain this structure, we can generate two equivalent hybrid orbitals on each C atom by combining the 2*s* orbital of carbon and any one of the three degenerate 2*p* orbitals.

By taking the sum and the difference of C 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 3.

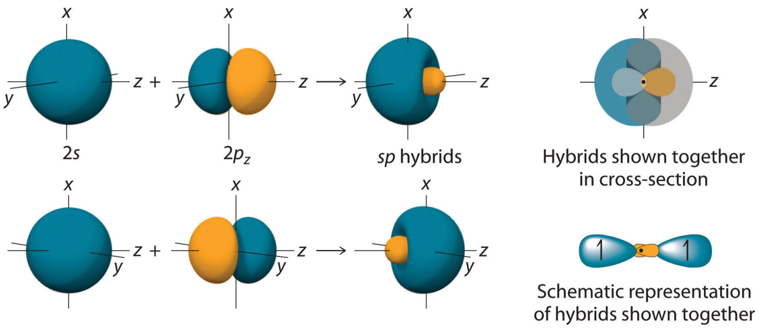
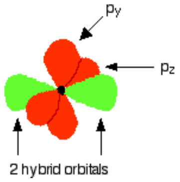


Figure 3: *The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180° to each other.*

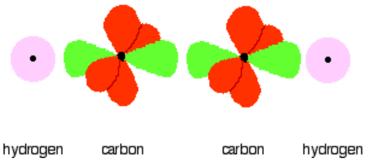
The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital.

One *sp* hybrid orbital on each C atom can now form a sigma bond with one of the H atoms. The other *sp* hybrid orbital on each C atom can overlap to form a sigma bond between the two C atoms. Both C atoms have two 2p orbitals that have yet to be used for bonding. These orbitals are perpendicular to each other on each C atom, but when the C atoms form a sigma bond and are pulled close together, two pi bonds can also form between the two C atoms because one set of p-orbitals can overlap above and below the internuclear axis, and the other set of p orbitals can overlap in front of and behind the internuclear axis.

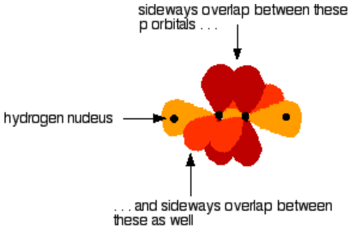
The entire bonding process looks like this (with the sp hybrid orbitals in bright green and the unhybridized p orbitals in red):



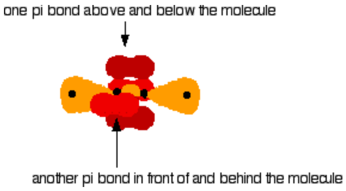
Notice that the two green lobes are two different hybrid orbitals - arranged as far apart from each other as possible. Do not confuse them with the shape of a p orbital. The two carbon atoms and two hydrogen atoms would look like this before they joined together:



The various atomic orbitals which are pointing towards each other now merge to give molecular orbitals, each containing a bonding pair of electrons. These are sigma bonds - just like those formed by end-to-end overlap of atomic orbitals in, say, ethane. The sigma bonds are shown as orange in the next diagram. The various p orbitals (now shown in slightly different reds to avoid confusion) are now close enough together that they overlap sideways.



Sideways overlap between the two sets of p orbitals produces two pi bonds - each similar to the pi bond found in, say, ethene. These pi bonds are at 90° to each other - one above and below the molecule, and the other in front of and behind the molecule. Notice the different shades of red for the two different pi bonds.



Example 1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur hybridizes its 3*s* and 3*p* orbitals, to produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon hybrides its 2*s* and 2*p* orbitals, to form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion
b. hydrazine ($H_2N–NH_2$)

Answer a

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Answer b

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom, and thu sthe same as the number of "things attached" to the central atom.

Hybridization Using d Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals, but we will not discuss the formation of the hybrid orbitals involving d orbitals.

Summary

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The combination of one *s* and one *p* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of one *s* and two or three *p* orbitals produces three equivalent **sp^2 hybrids** or four equivalent **sp^3 hybrids**, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

Contributors

Jim Clark (Chemguide.co.uk)

Modified by Tom Neils (Grand Rapids Community College)

3.11 Practice Problems

Chemical Formulas

1. For the following molecules; write the chemical formula, determine how many atoms are present in one molecule/formula unit, determine the molar mass, determine the number of moles in 1.00 gram, and the number of grams in exactly 5.00 x 10^{-2} moles.

a) carbon dioxide

b) iron (II) chloride

c) dinitrogen pentoxide

d) iron (III) sulfate

Exercise 1

Answers to Q1

Answer

Formula	Atoms per Molecule/Formula Unit	Molar Mass	Moles in 1.00 g	Grams in 5.00 x 10^{-2} moles
CO_2	3	44.01	2.27 x 10^{-2}	2.20
$FeCl_2$	3	126.75	7.89 x 10^{-3}	6.34
N_2O_5	7	108.02	9.26 x 10^{-3}	5.40
$Fe_2(SO_4)_3$	17	399.88	2.50 x 10^{-3}	20.0

2. Name the following compounds, determine the molar mass, determine how many O atoms are present in one molecule/formula unit, determine the grams of oxygen in 1.00 mole of the compound, and determine how many moles of O atoms in 8.35 grams of the compound.

a) K_2CO_3

b) $Ca(NO_3)_2$

c) Cu_2SO_4

d) N_2O

Exercise 2

Answers to Q2

Answer

Name	Molar mass	Atoms O per Molecule/Formula Unit	Grams of O in 1.00 mole	Moles of O in 8.35 grams
potassium carbonate	138.205	3	48.0	1.81 x 10^{-1}
calcium nitrate	164.088	6	96.0	3.05 x 10^{-1}
copper(I) sulfate	223.25	4	64.0	1.50 x 10^{-1}
dinitrogen monoxide	44.013	1	16.0	1.90 x 10^{-1}

3. Give the chemical formula (including the charge!) for the following ions. Also, write out the chemical formula for the compound each anion would form with K^+ and with Ca^{2+}.

a) sulfate

b) sulfite

c) nitrate

d) chloride

e) nitride

f) acetate

g) carbonate

Exercise 3

Answers to Q3

Answer

a) SO_4^{2-}; K_2SO_4; $CaSO_4$

b) SO_3^{2-}; K_2SO_3; $CaSO_3$

c) NO_3^-; KNO_3; $Ca(NO_3)_2$

d) Cl^-; KCl; $CaCl_2$

e) N^{3-}; K_3N; Ca_3N_2

f) $C_2H_3O_2^-$; $KC_2H_3O_2$; $Ca(C_2H_3O_2)_2$

g) CO_3^{2-}; K_2CO_3; $CaCO_3$

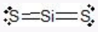
Lewis Dot Structures

4. For the compounds i) SiS_2, ii) PI_3, iii) SCl_2, and iv) CH_2PH a) draw the Lewis dot structure, b) determine the hybridization of the central atom(s), c) determine the EGA around the central atom(s), d) determine the MG around the central atom(s), e) determine the bond angles in the molecule, f) determine if the molecule is polar or non-polar

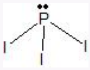
Exercise 4

Answers to Lewis dot questions

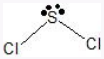
Answer

i) a) 

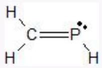
b) sp c) line d) line e) 180^{o} f) nonpolar

ii) a) 

b) sp^3 c) tetrahedron d) trigonal pyramid e) <109.5^{o} f) polar

iii) a) 

b) sp^3 c) tetrahedron d) bent e) <109.5^{o} f) polar

iv) a) 

b) C sp^2 and N sp^2 c) C and N trigonal plane d) C trigonal plane; N bent e) <120^{o} f) polar

Modified by Tom Neils (Grand Rapids Community College)

CHAPTER OVERVIEW

4: Intermolecular Forces, Phases, and Solutions

4.1 Water in Zero Gravity - an Introduction to Intermolecular Forces

Here on Earth, we all live in a state of gravity. Not only us, but everything around us, including water, is being pulled towards the center of the planet by gravity. True, it is nice that our dogs don't float off into space, but when a child drops their ice cream (which is full of water, by the way) they don't have to know about gravity to be upset.

***Floating Water in Zero Gravity**: Once again, astronauts on the International Space Station dissolved an effervescent tablet in a floating ball of water, and captured images using a camera capable of recording four times the resolution of normal high-definition cameras. The higher resolution images and higher frame rate videos can reveal more information when used on science investigations, giving researchers a valuable new tool aboard the space station. This footage is one of the first of its kind. The cameras are being evaluated for capturing science data and vehicle operations by engineers at NASA's Marshall Space Flight Center in Huntsville, Alabama.*

If you go far enough out in space, for instance, onto the International Space Station, gravity becomes negligible, and the laws of physics act differently than here on Earth. Just how might water act in a place of zero gravity? This video above from NASA gives you a good idea of how different water behaves when the effects if gravity are counteracted.

Actually, on the International Space Station, there is plenty of gravity—according to NASA scientists, the pull of Earth's gravity on the space station and its occupants is substantial: about 90 percent of the force at the Earth's surface. But since the space station is continuously falling around our planet, the astronauts and objects on board are in a kind of free-fall, too, and feel nearly weightless. Water on the space station behaves as if in a zero-gravity environment.

This unique picture shows not only a water drop but also an air bubble inside of the water drop. Notice they both behave the same....according to the laws of physics in space. They both form spheres. This makes sense, as without gravity to tug downward, the forces governing the objects are all the same. So, the water drop (and air bubble) form themselves so they occupy a shape having the least amount of surface area, which is a sphere. On Earth, gravity distorts the shape, but not in space.

Consider what would happen on Earth: The air bubble, lighter than water, would race upward to burst through the surface of the droplet. In space, the air bubble doesn't rise because it is no lighter than the water around it—there's no buoyancy. The droplet doesn't fall from the leaf because there's no force to pull it off. It's stuck there by molecular adhesion.

Sticky water. No buoyancy. These are some of the factors space-farers must take into account when they plan their space gardens. If water is sprayed onto the base of the plant will it trickle down to the roots? More likely it will stick to the stem or adhere to the material in which the plant grows. As humans spend more time and go farther out in space in the future, the physics of "space water" will need to be well understood.

Reference

- The Physics of Space Gardens, NASA.

4.2 Intermolecular Forces

Skills to Develop

- To describe the six types of intermolecular forces

In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together within molecules and polyatomic ions, *inter*molecular forces exist bewteen separate particles holding them next to each other, leading to the existence of the liquid and solid phases. Intermolecular forces are generally much weaker than bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids but are more similar to solids.*

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we first consider three kinds of intermolecular interactions that are the only types that can occur in pure substances (although they can also occur in mixtures): London forces, dipole/dipole forces, and hydrogen bonding. We will then discuss the three additional types of intermolecular electrostatic interaction that only occur in mixtures: ion–induced dipole interactions, dipole-induced dipole interactions, and ion–dipole interactions. See ***Figure* 1**.

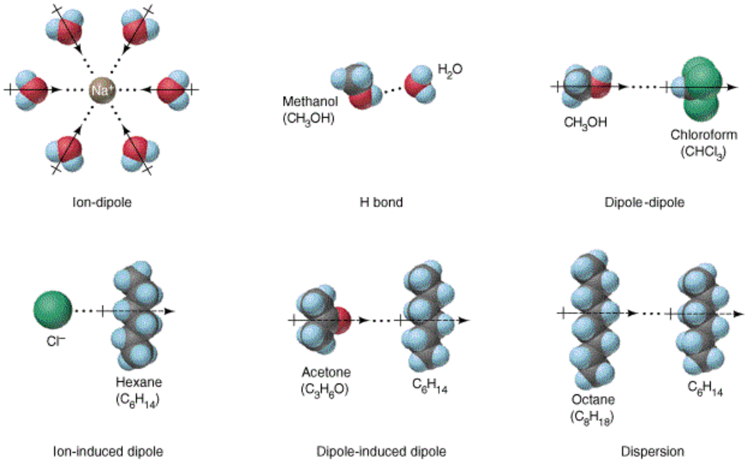


***Figure* 1**: *The six intermolecular forces*

London Dispersion Forces

Many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 1). What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances. (London forces also are exerted by polar molecules because these molecules can also experience temporary fluctuations in their electron distributions.)

Table* 1*: *Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds*

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

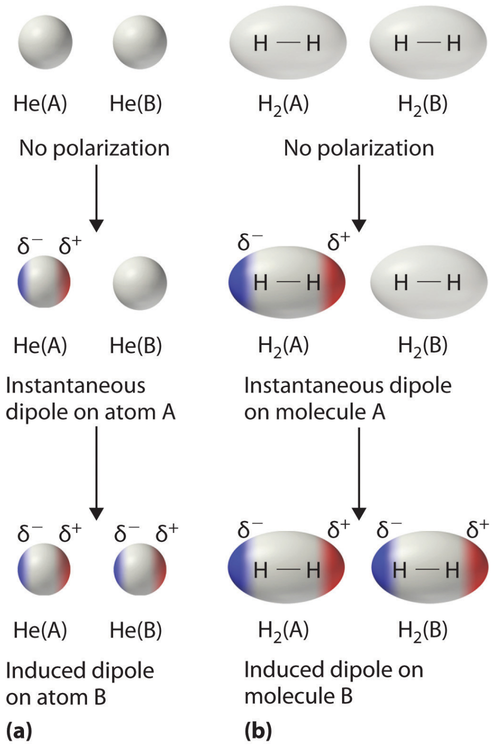


***Figure 2**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.*

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 2, tends to become more pronounced as atomic and molecular masses increase (Table 1). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 3). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 3 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

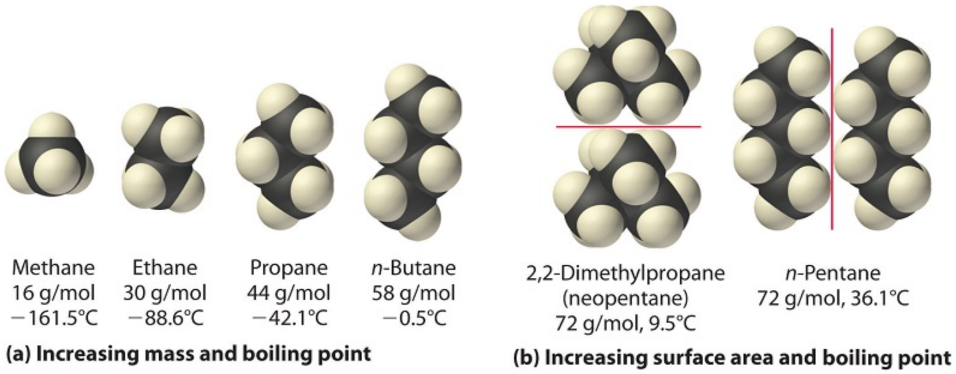


Figure 3: *Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear n-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas n-pentane is a volatile liquid.*

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 1

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise 1

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure $4a$.

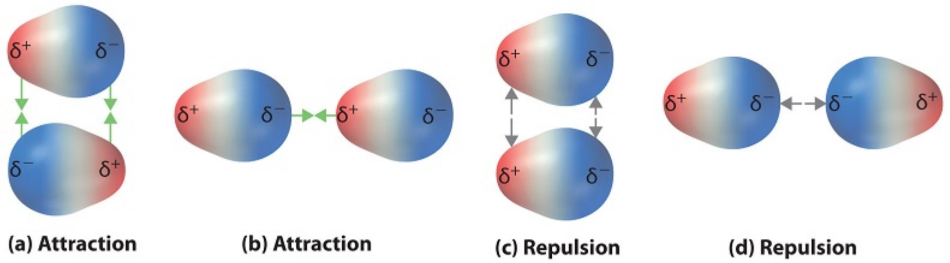


Figure 4: *Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 4c). Hence dipole–dipole interactions, such as those in Figure 4b, are *attractive intermolecular interactions*, whereas those in Figure 4d are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 5. On average, however, the attractive interactions dominate.

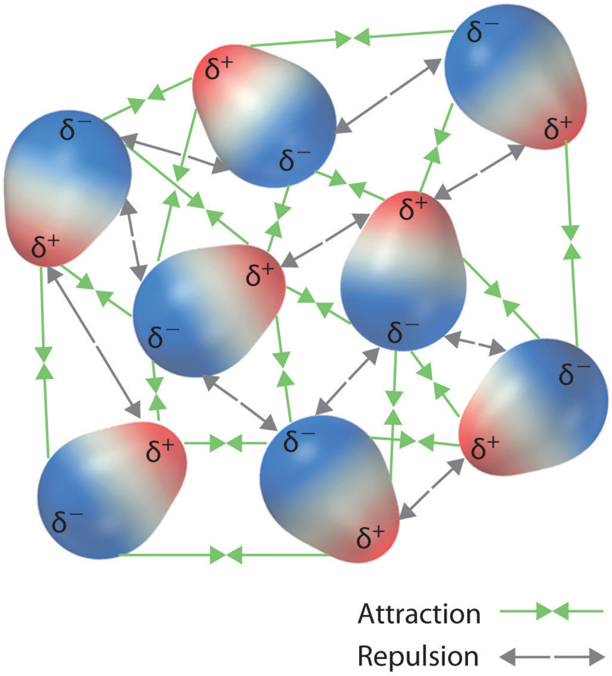


Figure 5: *Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules*

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas $NaCl$, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 2.

Table 2*: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass*

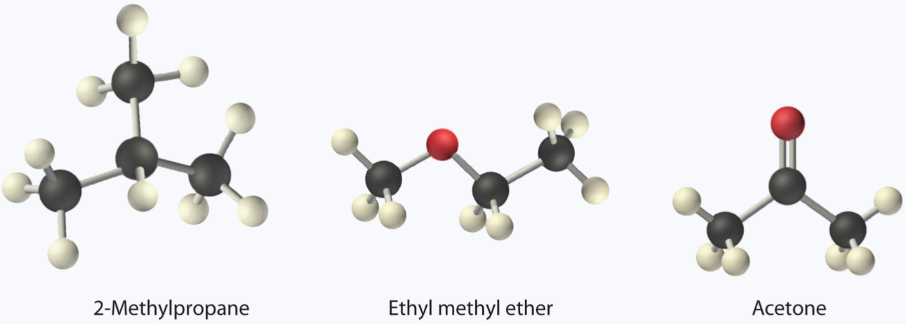
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*

Example 2

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone.

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 2

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S=O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 6. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

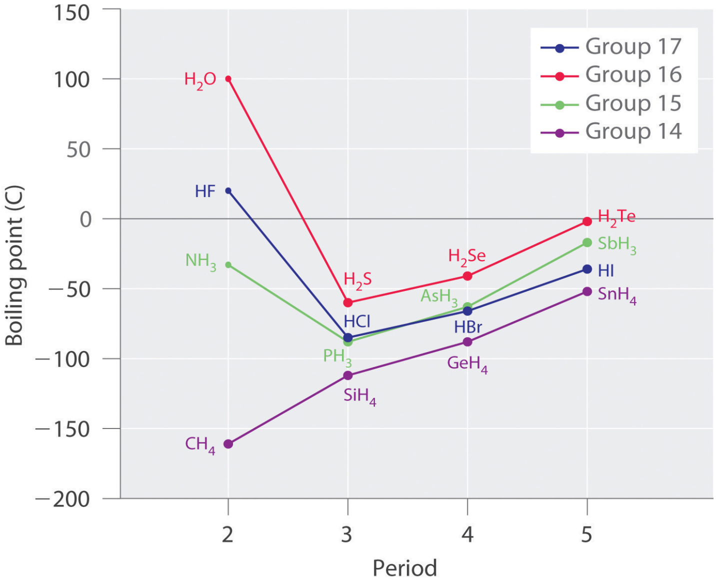


***Figure 6:** The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.*

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 7. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F and the O, N, orF atom that has the lone pair of electrons. Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O⋯H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

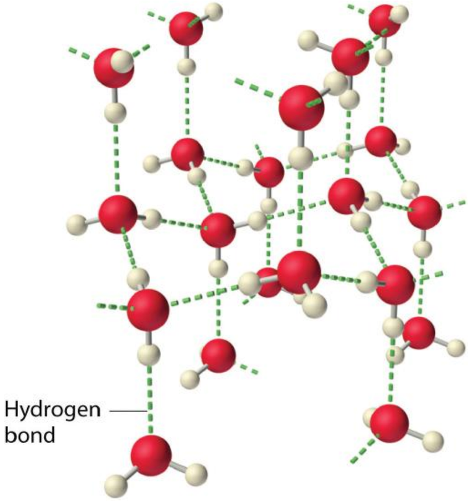


***Figure 7**: The Hydrogen-Bonded Structure of Ice.*

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds as a pure substance? Draw the hydrogen-bonded structures.

Given: compounds

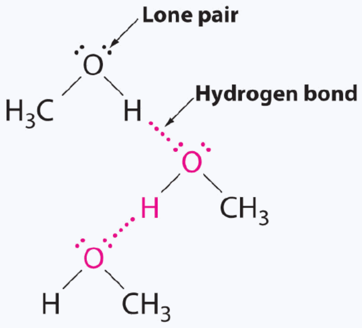
Asked for: formation of hydrogen bonds and structure

Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot form hydrogen bonds as a pure substance. The one compound that can form hydrogen bonds, methanol (CH_3OH), contains both a hydrogen atom attached to O and two lone pairs of electrons on O; methanol can thus form hydrogen bonds. The hydrogen-bonded structure of methanol is as follows:



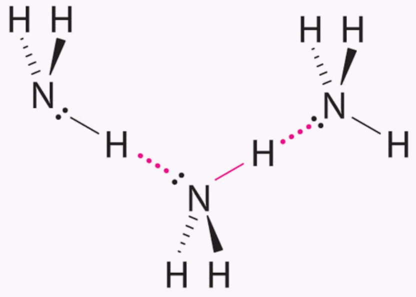
Hydrogen bonding in methanol

Exercise 3

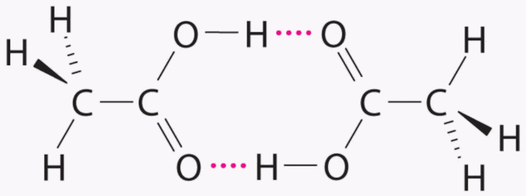
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds as a pure substance? Draw the hydrogen-bonded structures.

Answer:

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

To predict the relative boiling points of the compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269°\text{C}) < \text{Ar } (-185.7°\text{C}) < N_2O\ (-88.5°\text{C}) < C_{60}\ (>280°\text{C}).$$

Exercise 4

Arrange 2,4-dimethylheptane, Ne, CS_2, and Cl_2 in order of decreasing boiling points.

Answer:

2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Example 5:

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.

b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 5

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Intermolecular Forces in Mixtures

When you have mixtures, you can have a combination of ions, polar molecules, and nonpolar molecules. If the mixture contains all nonpolar molecules, then the only IMFs in that mixture will be London forces. An example of such a mixture would be hexane (C_6H_{14}) and benzene (C_6H_6):

If the mixture contains only polar molecules, then there will be London forces, dipole/dipole forces, and possibly hydrogen bonding. For example, in a mixture of acetone and diethyl ether, the polar ether and acetone molecules would exert London forces and dipole/dipole forces:

In a mixture of acetone and methanol, there would be London forces, dipole/dipole forces, and hydrogen bonding between the acetone and methanol molecules:

If the mixture contains different types of particles, these particles will form electrostatic interactions, but they will involve one or more of the following IMFs.

Dipole/Induced Dipole Forces

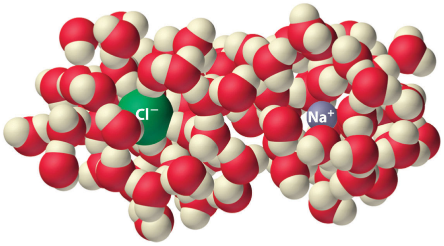
In a mixture of polar and nonpolar molecules, there will be London forces, but also dipole/induced dipole forces. These forces are created when the polar molecules get close enough to the nonpolar molecules to distort the electron clouds of the nonpolar molecules and create temporarily induced dipoles. These forces are usually quite weak, but their strength depends on the number of valence electrons and on the polarity of the polar molecule. In a solution of ethanol and hexane (yes, they do form a solution) there would be London forces and dipole induced dipole forces as the ethanol molecules induce dipoles in the benzene molecules:

Ion/Induced Dipole Forces

In a mixture of ions and nonpolar molecules, there will be London forces, but also ion/induced dipole forces. These forces are created when the ions get close enough to the nonpolar molecules to distort the electron clouds of the nonpolar molecules and create temporarily induced dipoles. These forces are usually quite weak, but their strength depends on the number of valence electrons and on the charge on the ion. These are not common forces, because ions and nonpolar molecules do not mix well, however, in biochemical systems these interactions can be common. In blood, Fe^{2+} ions in hemoglobin complexes induce dipoles in oxygen molecules to create ion/induced dipole forces so that O_2 molecules can be carried through the bloodstream:

Ion/dipole Forces

In a mixture of ions and polar molecules, there will be London forces, but also ion/dipole forces. These forces are **by far** the strongest intermolecular forces, and their strength can often surpass the strength of some weak covalent bonds. These forces form when ions and polar molecules get close to each other. Ions are most strongly attracted to water molecules, because of the high polarity of the water molecules, but other small, very polar molecules such as methanol (CH_3OH), ethanol (CH_3CH_2OH), and dimethylsulfoxide (DMSO, $(CH_3)_2SO$) can also dissolve ions and form ion/dipole forces. In a solution of sodium chloride and water there would be London forces and ion/dipole forces as the water molecules surround the sodium and the chloride ions:



Summary

Intermolecular forces are electrostatic in nature. Separate molecules are held close to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The six types of intermolecular interactions are London dispersion forces, dipole–dipole interactions, hydrogen bonding, dipole/induced dipole forces, ion/induced dipole forces, and ion/dipole forces. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules. Because of strong O⋯H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water. **Dipole/induced dipole forces** occur only in mixtures of polar and nonpolar substances, and the forces are generally weak. **Ion/induced dipole forces** are less common than dipole/induced dipole forces, simply because ions and nonpolar molecules do not mix well. **Ion/dipole forces** are the strongest intermolecular forces, and they allow many ionic compounds to dissolve in water.

Modified by Tom Neils (Grand Rapids Community College)

4.3 Application of IMFs: Evaporation, Vapor Pressure, and Boiling Points

Skills to Develop

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure $4.3 ApplicationofIMFs.1$), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

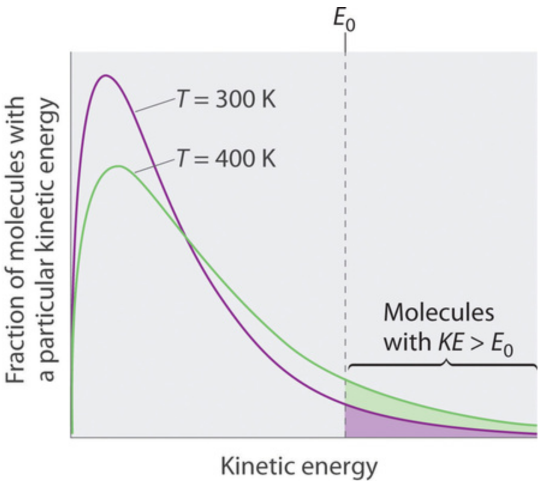


Figure $4.3 ApplicationofIMFs.1$: *The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.*

To understand the causes of vapor pressure, consider the apparatus shown in Figure $4.3 ApplicationofIMFs.2$ When a liquid is introduced into an evacuated chamber (part (a) in Figure $4.3 ApplicationofIMFs.2$), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

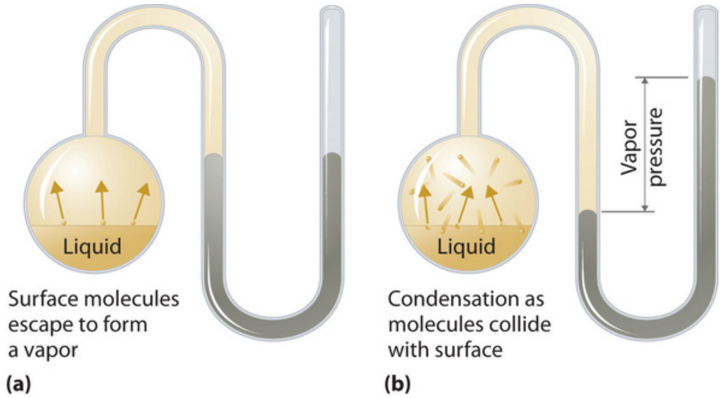


Figure $4.3 Application of IMFs.2$: *Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.*

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure $4.3 Application of IMFs.2$). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure $4.3 Application of IMFs.3$

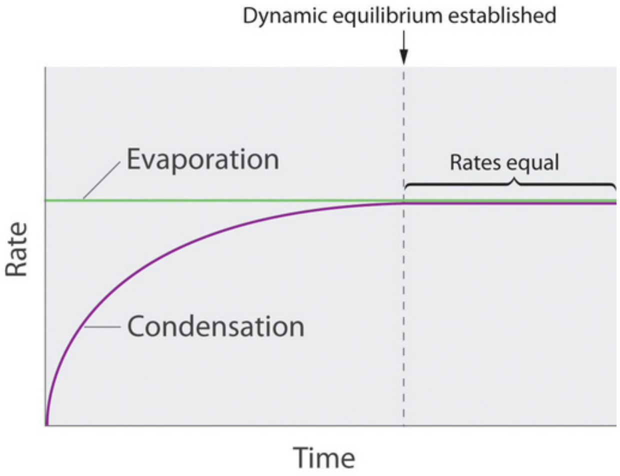


Figure $4.3 Application of IMFs.3$*: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.*

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure $4.3 Application of IMFs.4$) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

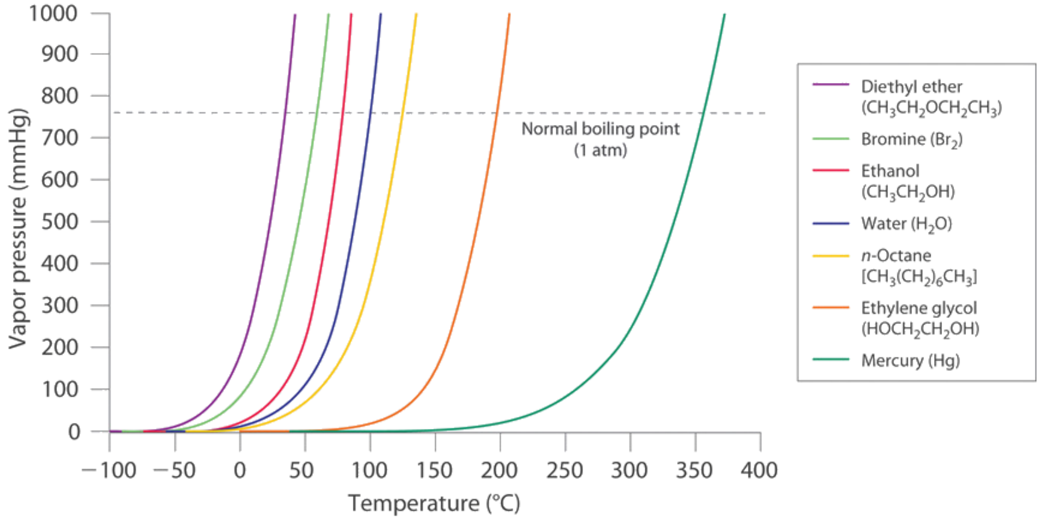


Figure $4.3 Application of IMFs.4$: *The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid.*

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point (Table 11.4). It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure $4.3 Application of IMFs.4$ Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won’t explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure $4.3 Application of IMFs.4$ are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table $4.3 Application of IMFs.1$: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table $4.3 Application of IMFs.1$lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

Example $4.3 Application of IMFs.2$: Boiling Mercury

Use Figure $4.3 Application of IMFs.4$to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C

Mercury boils at 356 °C at room pressure. To see video go to https://www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure $4.3 Application of IMFs.4$, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure $4.3 Application of IMFs.4$and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx$ 75 mmHg. Hence this is the pressure required for mercury to boil at 250°C.

Exercise $4.3 Application of IMFs.2$: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure $4.3 Application of IMFs.4$ to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

Contributors

- Modified by Joshua Halpern (Howard University)
- Modified by Tom Neils (Grand Rapids Community College)

4.4: Intermolecular Forces in Action: Surface Tension, Viscosity, and Capillary Action

Skills to Develop

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then, do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic (electrostatic) bonds has as surface tension that is 15-times higher: 4.86 x 10^{-1} J/m^2 (at 20°C).

Figure $4.4.1$ presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads (see the chapter opener photo). A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

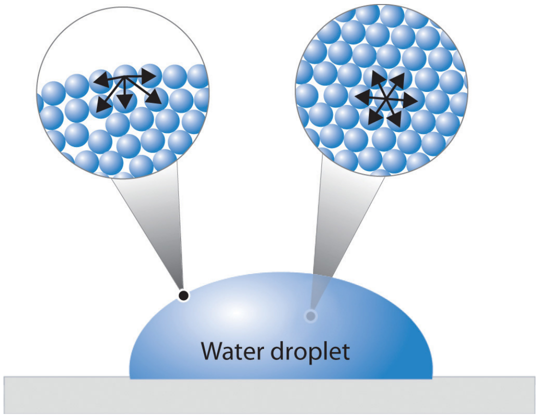


Figure $4.4.1$: *A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.*

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it "floats," even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even better describe in the zero gravity conditions of space as Figure $4.4.2$ indicates (and more so in the video link).

***Figure 4.4.2**: The Effects of the High Surface Tension of Liquid Water. The Full video can be found at https://www.youtube.com/watch?v=9jB7rOC5kG8.*

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 4.4.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

***Table 4.4.1**: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids*

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 4.4.3.

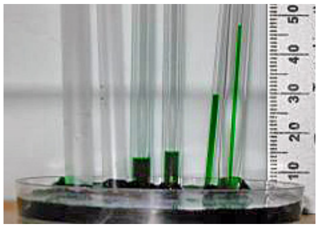


Figure 4.4.3: *The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.*

When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure 4.4.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure 4.4.4).

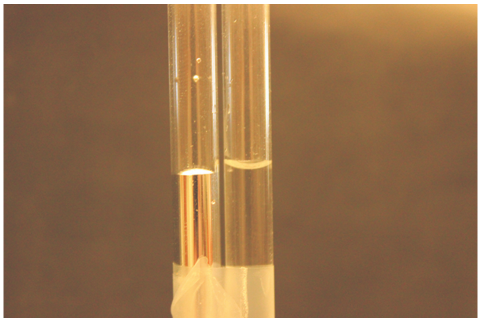


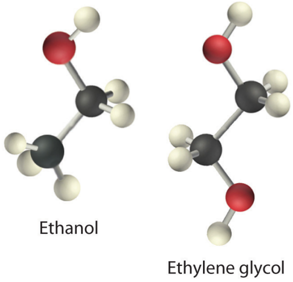
Figure 4.4.4: *The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)*

Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and "wick" the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become "tangled" with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too "thin" (have too low a viscosity) to be effective at high temperatures.

Figure 4.4.5: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure 4.4.5). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives "for improved engine performance" are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 4.4.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise 4.4.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

Modified by Tom Neils (Grand Rapids Community College)

4.5: Solids, Liquids, and Gases: A Molecular Comparison

Skills to Develop

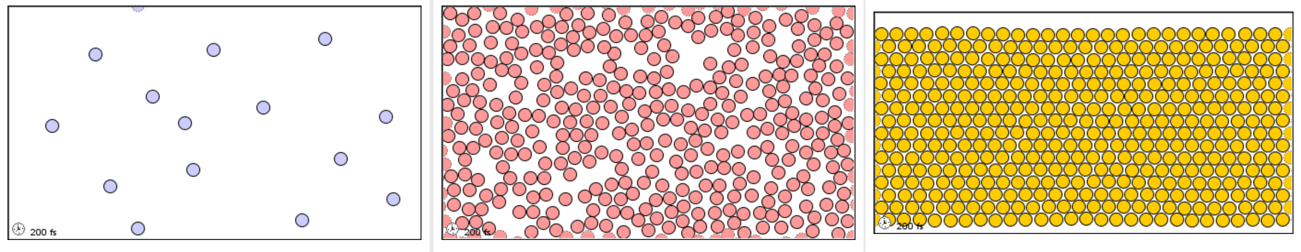
- To be familiar with the kinetic molecular description of liquids.

The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *Covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

Figure 4.5.1: *The four fundamental states of matter. Clockwise from top left, they are solid, liquid, plasma, and gas, represented by an ice sculpture, a drop of water, electrical arcing from a tesla coil, and the air around clouds, respectively. Images used with permission from Wikipedia.*

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance and the intermolecular forces try to draw the particles together (Table 4.5.2). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the effectiveness of intermolecular forces

***Table 4.5.2**: Molecular level picture of gases, liquids and solids.*



(a) in the gaseous state | *(b) as a liquid* | (c) *in solid form*

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of effective attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit ***non-ideal*** behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gases
- Liquids have a definite volume, independent of the size and shape of their container

- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

> *Thus, liquids can be poured and assume the shape of their containers*

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in relatively stable positions
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

> *Due to the strong intermolecular forces between neighboring molecules, solids are rigid*

- Cooling a gas may change the state to a liquid
- Cooling a liquid may change the state to a solid
- Increasing the pressure on a gas may change the state to a liquid
- Increasing the pressure on a liquid may change the state to a solid

***Video* $4.5.1$**: *Video highlighting the properties for the three states of matter. Source found at https://www.youtube.com/watch?v=s-KvoVzukHo.*

Physical Properties of Liquids

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described previously This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers. A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces. Solids and liquids have particles that are fairly close to one another, and are thus called "**condensed phases**" to distinguish them from gases

- **Density**: The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.
- **Molecular Order:** Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids, the molecules in liquids are not

arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.

- **Compressibility**: Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.
- **Thermal Expansion**: The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table S1 (with a shorten version in Table $4.5.1$) that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

***Table* $4.5.1$**: *The Density of Water at Various Temperatures*

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.
- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 11.1.3).

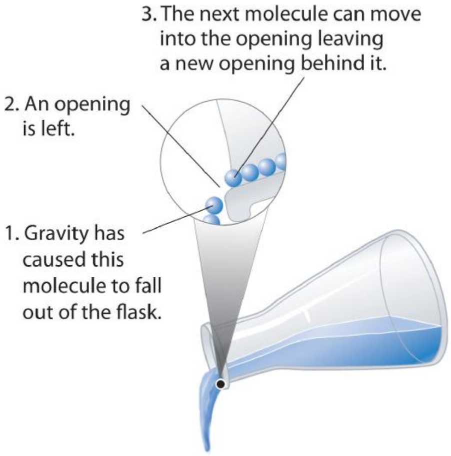


Figure* $4.5.3$*: *Why Liquids Flow. Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container.*

Contributors

- Mike Blaber (Florida State University)
- Modified by Tom Neils (Grand Rapids Community College)

4.6 Phase Changes

We have previously described **evaporation**, the change of a liquid to a gas. This process is always endothermic, because energy is required to completely disrupt the IMFs of attraction between the particles. The reverse process of evaporation is **condensation**, which is always an exothermic process because IMFs of attraction form among the particles as they congregate into droplets. The phase changes involving solids are described below.

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure 1). The reverse of sublimation is called **deposition**, a process in which gaseous substances directly change into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

Figure* 1*: *Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)*

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔHsub, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H_{\text{sub}} = 26.1\ \mathrm{kJ/mol} \tag{1}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \quad \Delta H_{\text{dep}} = -\Delta H_{\text{sub}} = -26.1\ \mathrm{kJ/mol} \tag{2}$$

Fusion/Melting and Solidification/Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure \(\PageIndex{2}\).

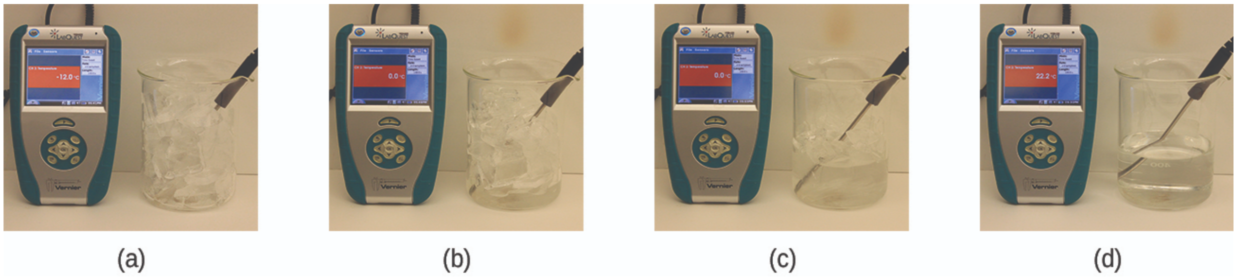


Figure 2: *(a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).*

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal process of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O_{(\mathit{s})} \rightarrow H_2O_{(\mathit{l})}} \quad \Delta H_{\text{fus}} = 6.01\ \mathrm{kJ/mol} \tag{3}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O_{(\mathit{l})} \rightarrow H_2O_{(\mathit{s})}} \quad \Delta H_{\text{frz}} = -\Delta H_{\text{fus}} = -6.01\ \mathrm{kJ/mol} \tag{4}$$

Selected molar enthalpies of fusion are tabulated in Table 1. Solids like ice which have strong intermolecular forces have much higher values than those like CH_4 with weak ones. Note that the enthalpies of fusion and vaporization change with temperature.

Table 1: *Molar Enthalpies of Fusion and Vaporization of Selected Substances.*

Substance	**Formula**	**ΔH(fusion) / kJ mol^1**	**Melting Point / K**	**ΔH(vaporization) / kJ mol^{-1}**	**Boiling Point / K**	**($\Delta H_v/T_b$) / JK^{-1} mol^{-1}**
Neon	Ne	0.33	24	1.80	27	67
Oxygen	O_2	0.44	54	6.82	90.2	76
Methane	CH_4	0.94	90.7	8.18	112	73
Ethane	C_2H_6	2.85	90.0	14.72	184	80
Chlorine	Cl_2	6.40	172.2	20.41	239	85
Carbon tetrachloride	CCl_4	2.67	250.0	30.00	350	86
Water*	H_2O	6.00678 at 0°C, 101kPa 6.354 at 81.6 °C, 2.50 MPa	273.1	40.657 at 100 °C, 45.051 at 0 °C, 46.567 at -33 °C	373.1	109
n-Nonane	C_9H_{20}	19.3	353	40.5	491	82
Mercury	Hg	2.30	234	58.6	630	91

Substance	Formula	ΔH(fusion) / kJ mol^{1}	Melting Point / K	ΔH(vaporization) / kJ mol^{-1}	Boiling Point / K	($\Delta H_v/T_b$) / JK^{-1} mol^{-1}
Sodium	Na	2.60	371	98	1158	85
Aluminum	Al	10.9	933	284	2600	109
Lead	Pb	4.77	601	178	2022	88

*http://www1.lsbu.ac.uk/water/data.html

Energy Changes Associated with Phase Changes

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess’s Law.

$$\begin{array}{c}
\text{solid} \longrightarrow \text{liquid} \quad \Delta H_{\text{fus}} \\
\underline{\text{liquid} \longrightarrow \text{gas} \quad \Delta H_{\text{vap}}} \\
\text{solid} \longrightarrow \text{gas} \quad \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}
\end{array} \tag{5}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 3. For example:

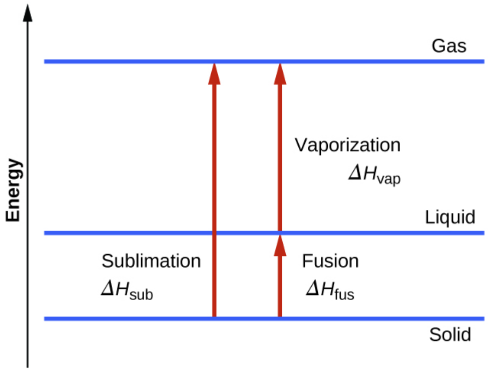


***Figure 3**: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.*

Contributors

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

4.7: Pressure: The Result of Particle Collisions

Skills to Develop

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

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 $4.7.1$). 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.

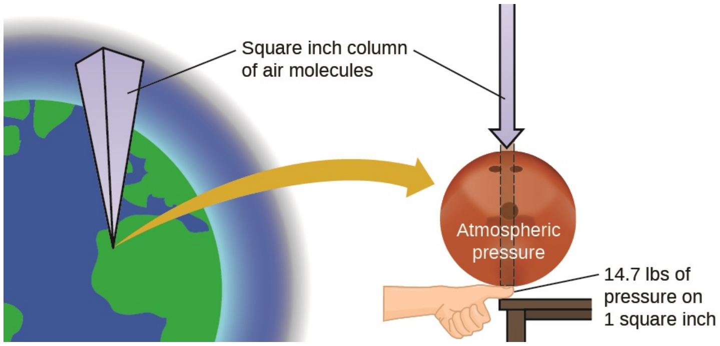


***Figure* $4.7.1$**: *The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.*

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.

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.

Pressure is defined as the force exerted on a given area:

$$P = \frac{F}{A} \tag{4.7.1}$$

Since pressure is directly proportional to force and inversely proportional to area (Equation $4.7.1$), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 4.7.1) to determine which would be more likely to fall through thin ice in Figure 4.7.2.—the elephant or the figure skater?

***Figure 4.7.2**: 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 her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).*

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:

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2 \tag{4.7.2}$$

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:

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2 \tag{4.7.3}$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall though thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2 \tag{4.7.4}$$

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 4.7.1 provides some information on these and a few other common units for pressure measurements

***Table 4.7.1:** Pressure Units*

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
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	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

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
torr	$1 \text{ torr} = \frac{1}{760} \text{ atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

Example 4.7.1: 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 9.2.1.

a. $29.2 \text{ in } \cancel{\text{Hg}} \times \frac{25.4 \text{ } \cancel{\text{mm}}}{1 \text{ } \cancel{\text{in}}} \times \frac{1 \text{ torr}}{1 \text{ mm } \cancel{\text{Hg}}} = 742 \text{ torr}$

b. $742 \text{ } \cancel{\text{torr}} \times \frac{1 \text{ atm}}{760 \text{ } \cancel{\text{torr}}} = 0.976 \text{ atm}$

c. $742 \text{ } \cancel{\text{torr}} \times \frac{101.325 \text{ kPa}}{760 \text{ } \cancel{\text{torr}}} = 98.9 \text{ kPa}$

d. $98.9 \text{ } \cancel{\text{kPa}} \times \frac{1000 \text{ } \cancel{\text{Pa}}}{1 \text{ } \cancel{\text{kPa}}} \times \frac{1 \text{ } \cancel{\text{bar}}}{100,000 \text{ } \cancel{\text{Pa}}} \times \frac{1000 \text{ mbar}}{1 \text{ } \cancel{\text{bar}}} = 989 \text{ mbar}$

Exercise 4.7.1

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 4.7.3). 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.

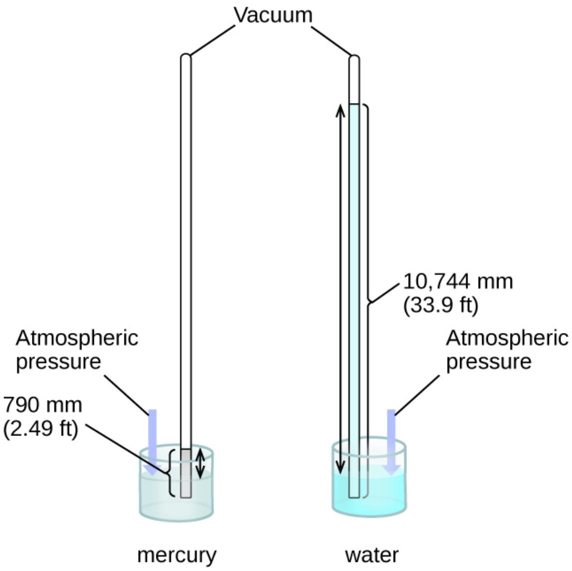


***Figure 4.7.3**: In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.*

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 $\frac{1}{13.6}$ 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. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, p:

$$p = h\rho g \tag{4.7.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

Example 4.7.2: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = 13.6 g/cm^3.

Solution

The hydrostatic pressure is given by Equation 4.7.5, with $h = 760\,mm$, $\rho = 13.6\,g/cm^3$, and $g = 9.81\,m/s^2$. Plugging these values into the Equation 4.7.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\mathrm{m}^2 = 101,325\ \frac{\mathrm{kg\cdot m/s^2}}{\mathrm{m^2}} = 101,325\ \frac{\mathrm{kg}}{\mathrm{m\cdot s^2}} \tag{4.7.6}$$

$$\begin{aligned} p &= \left(760\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right) \times \left(\frac{13.6\ \mathrm{g}}{1\ \mathrm{cm^3}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{(100\ \mathrm{cm})^3}{(1\ \mathrm{m})^3}\right) \times \left(\frac{9.81\ \mathrm{m}}{1\ \mathrm{s^2}}\right) \\ &= (0.760\ \mathrm{m})(13,600\ \mathrm{kg/m^3})(9.81\ \mathrm{m/s^2}) = 1.01 \times 10^5\ \mathrm{kg/ms^2} = 1.01 \times 10^5\, N/\mathrm{m}^2 \\ &= 1.01 \times 10^5\ \mathrm{Pa} \end{aligned}$$

Exercise 4.7.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

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 $4.7.3$) 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.

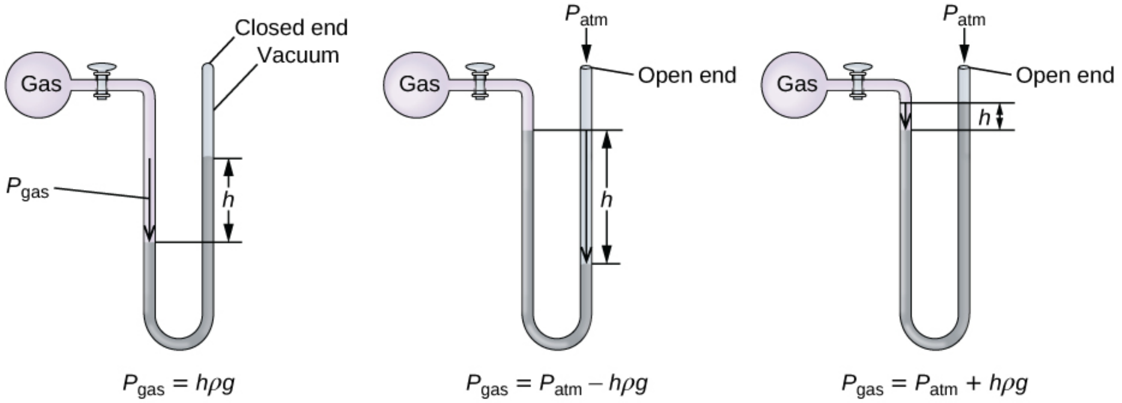
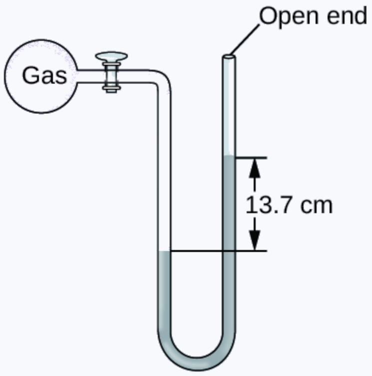


Figure 4.7.4: *A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.*

Example $4.7.3$: Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown below. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

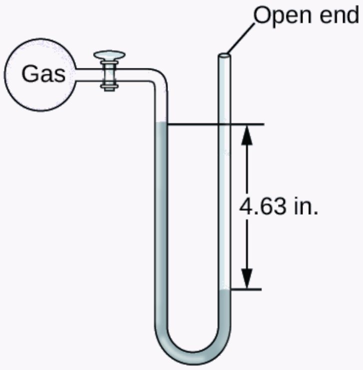
b. $897\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 1.18\ \text{atm}$

c. $1.18\ \cancel{\text{atm}} \times \frac{101.325\ \text{kPa}}{1\ \cancel{\text{atm}}} = 1.20 \times 10^2\ \text{kPa}$

Exercise 4.7.3

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Answer a

642 mm Hg

Answer b

0.845 atm

Answer c

85.6 kPa

Application: 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 4.7.5). 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 4.7.5**: (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)*

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 4.7.5) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

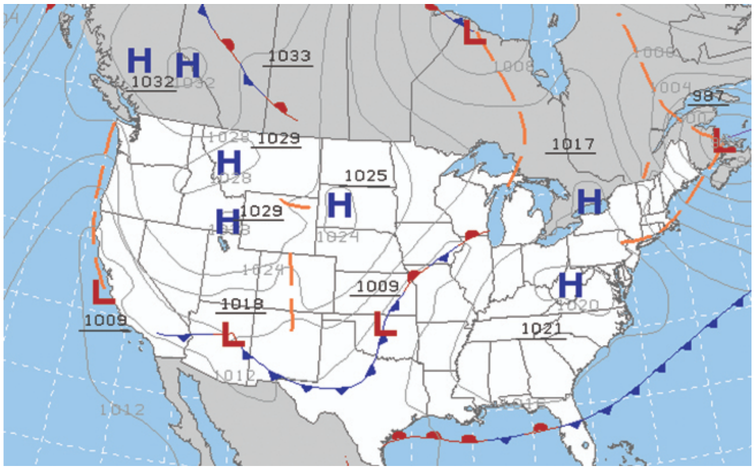


***Figure 4.7.6**: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric 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 4.7.7: 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.

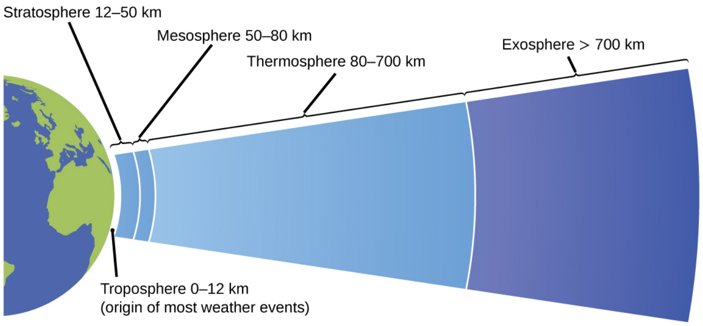


Figure 4.7.7: *Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.*

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.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Glossary

atmosphere (atm)
unit of pressure; 1 atm = 101,325 Pa

bar
(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
device used to measure atmospheric pressure

hydrostatic pressure
pressure exerted by a fluid due to gravity

manometer
device used to measure the pressure of a gas trapped in a container

pascal (Pa)
SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)
unit of pressure common in the US

pressure
force exerted per unit area

torr

unit of pressure; $1\ \text{torr} = \frac{1}{760}\ \text{atm}$

Contributors

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

4.8: Gases

The Ideal Gas Law

An ideal gas is a mythical substance in which the gas particles have neither volume nor attractive intermolecular forces. Such a substance does not exist, but using the approximation creates a very simple mathematical description of a gas sample, the ideal gas law. The ideal gas law, **PV = nRT**, relates the four variables that describe any sample of a gas:

> **P is pressure**, the force per unit area exerted by gas molecules as they bounce off of the surfaces that they hit. There are many units for measuring gas pressure. A unit you may have seen in a weather report is inches of mercury (in Hg), which are convenient units to use when measuring pressure with a mercury manometer. Another common unit is pounds per square inch (psi). However, we will use the unit of atmospheres (atm), an older pressure unit that was once defined as the pressure required to hold up a 760 mm column of Hg at 0^oC. Colloquially, 1.00 atm is the pressure exerted by the atmosphere at sea level on an average day.
>
> **V is for volume**, the amount of space that the gas sample is confined in. We will use the unit of Liters for our volume measurements.
>
> **n is for moles**, the number of moles of gas particles in the sample.
>
> **T is for temperature**, the property that allows us to determine the direction of heat flow and also gives us an idea of the kinetic energy of the gas molecules. We will use the Kelvin temperature scale for temperature, because we can not have any negative temperatures when describing gases. (Remember, the temperature in Kelvin = the temperature in Celsius plus 273.15^o. K = 273.15 + ^{o}C.)
>
> **R is the gas constant**, 0.08206 $\frac{L \cdot atm}{mole \cdot K}$. This value can be obtained from the ratio of $\frac{(22.4\ L)(1.00\ atm)}{(1.00\ mole)(273.15\ K)}$, employing the volume that 1.00 mole of an ideal gas occupies when held at 1.00 atm pressure and a temperature of 273.15 K, but it is true for any ideal gas under any set of conditions.

The ideal gas law is useful because if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*) for a sample of gas, we can calculate the value of the fourth variable for that gaseous sample. The equation also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 4.8.1

A balloon with a volume of 31,150 L is to be filled with an ideal gas. If the temperature at ground level is 303 K, and the atmospheric pressure is 0.980 atm, how many moles of hydrogen gas will be needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: moles of gas

Strategy:

1. Solve the ideal gas law for the unknown quantity, in this case *n*.
2. Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution

$$n = \frac{PV}{RT} = \frac{(0.980\ atm)(31150\ L)}{(0.08206\ \frac{L\ atm}{mole\ K})(303\ K)} = 1.23 \times 10^3 moles$$

Exercise 4.8.1

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.0250 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25.0°C?

Answer

1.51 L

A Practical Use of Air Pressure

A water well is an excavation or structure created in the ground by digging, driving, boring, or drilling to access groundwater in underground aquifers. The well water is often drawn by a pump (Figure $4.8.1$). Unfortunately, it impossible to pump water from very deep in the ground with just a surface pump. The key to understanding why is realizing that suction generated by the pump is not a force, but simply removing an opposing force to the force of air pressure which is already there. When you stick a pipe down a deep hole into a pool of water at the bottom of a well, air inside the pipe is pushing down on the water in the pipe, and air outside the pipe is pushing down on the water outside the pipe, which in turn pushes up on water inside the pipe - all is in a balance.

Figure $4.8.1$: *The manual water pump draws water up from a well by creating a vacuum that water rushes in to fill. Hand pump to pump water from a well in a village near Chennai in India. Image used with permission (CC BY 2.0; Sustainable Sanitation Alliance).*

Let's say you remove the air inside the pipe. The water is pushed up the the same as it was before, but there is no counter acting force pushing the water down, so the water begins to rise inside the pipe (Figure $4.8.2$). So far so good, but the water stops rising at some height because the water is pulled down by gravity (i.e., the more water in the pipe, the more it weighs). Because the force of the air outside the pipe is not changing, eventually the weight of the water is equal to the air pressure outside the pipe. When this happens, the system is in balance again and water stops flowing.

> *Suction is not a force. Atmospheric pressure is the force that pushes the water up the pipe*

Water is pumped from a well by creating a partial vacuum above the water by the pump. The amount of vacuum is equal to the weight of the column of water from the water table to the surface. Atmospheric pressure at sea level is 760 mm of mercury ($1.01 \times 10^5\ Pascals$), which is equivalent to a 10.3-meter column of water. This is how deep water can be pumped from (with a surface pump; other pressurized pumps can go deeper).

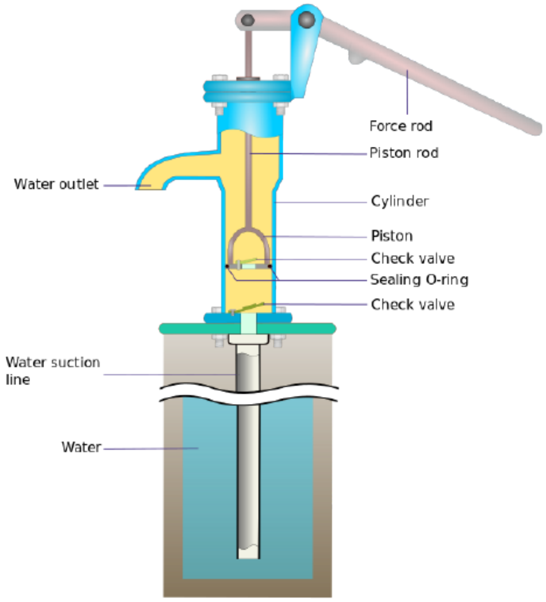


Figure 4.8.2: Cross section and details of a surface pump used in a well. Image used with permission (CC BY-SA 3.0; Manco Capac).

Template:HideTOC

Modified by Tom Neils (Grand Rapids Community College)

4.9 Solutions - What Mixes Together and Why

Solutions with Liquid Solvents

A solution is a homogeneous mixture in which the solute particles are so small that they cannot be filtered out and they do not scatter light. For a solution to form, there needs to be the correct combination of enthalpic (intermolecular forces) and entropic effects to enable the solvent and solute particles to interact strongly with each other without decreasing the entropy of the system. In this section we will closely examine the effects of enthalpy, but we will not spend too much time discussing the effects of entropy. To understand the effects of intermolecular forces, we need to go all the way back to bonds.

How Does Bond Polarity Affect/Determine Bond Type?

A bond is defined as the sharing of electrons by two atoms. Bond polarity occurs when two atoms share electrons unequally because of a difference in the strength of attraction for the shared electrons by the nuclei of the two different atoms. The strength of attraction scale that is most commonly used is electronegativity (EN). There are three common categories of bonds, based on the difference in electronegativity (ΔEN) values of the two bonding atoms:

a. If two atoms have identical, or similar EN values, their nuclei both pull on the shared electrons nearly equally. This equal sharing is called a nonpolar covalent bond – neither nucleus has a greater electron density after forming the bond than it did before forming the bond. Examples: H-H, F-F
b. If two atoms have a modest difference in EN values, the nucleus of the atom with the higher EN value has a greater pull on the shared electrons, so that these electrons are more likely to be found closer to that nucleus than the nucleus with the lower EN value. This unequal sharing is called a polar covalent bond – there is a partial negative charge around the nucleus of the atom with the higher EN value because it is "using/borrowing" the electron(s) of the atom with the lower EN value. This leaves a partial positive charge around the nucleus of the atom with the lower EN value because its electron(s) are less likely to be found near it. Examples: H-Cl, C-F
c. If two atoms have a large difference in EN values, the shared electrons are much more likely to be found closer to the nucleus of the atom with the higher EN value. There is always some small likelihood of finding the shared electron(s) near the nucleus of the atom with the smaller EN value, so there are never really separate, fully-charged ions in a sample of a pure substance. Nevertheless, it is common practice to designate these bonds as ionic bonds. This practice is reasonable because of the formation of separate, fully-charged ions when compounds involving these extremely polar bonds are placed in water. (See ion-dipole IMFs below.) Examples: Na-Cl, K-F

There are **many** approaches to the task of determining into which category a given bond should be placed. Some methods are more rigorous than others, but often the rigorous methods are too complicated to be used quickly and simply. You should find a method that you like and that serves your needs sufficiently and stick with it until you are asked to use a more rigorous method. The simplest method is that a bond between a metal and a nonmetal is ionic, whereas a bond between two nonmetals is covalent.

There are two common conventions used to show the polarity of a bond:

a. lower case deltas (δ^+ and δ^-): These two symbols must always be used together, because they show the partial positive pole and the partial negative pole of the polar bond. Example:

$$\overset{\delta^+}{\mathrm{B}} – \overset{\delta^-}{\mathrm{Cl}}$$

a. a dipole arrow ⟼ : This symbol is used to show the positive end of the dipole and the negative end at which the electron density is greatest. Example:

$$\overset{\longmapsto}{\mathrm{B} – \mathrm{Cl}}$$

What is Molecular Polarity?

The concept of molecular polarity is most easily applied to small molecules, but it can be applied to larger molecules with the understanding that larger molecules may have multiple “identities.” The first task in determining molecular polarity is to identify whether a substance is comprised of ions or of molecules. Individual small ions are not polar, because they do not have a charge separation that leads to the existence of a positive pole and a negative pole. Thus, if you identify a compound as consisting of ions (either monatomic or small polyatomic), you are no longer concerned about molecular polarity of that substance. To determine the molecular polarity of a compound that contains only covalent bonds, you need to consider three aspects of the molecule:

a. the shape of the molecule
b. the polarity of all of the bonds in the molecule
c. the presence of atoms with lone pairs.

Taking these three aspects into account, you should be able to determine if a small molecule is polar or nonpolar. Some helpful **shortcuts** that are almost always true:

a) If the central atom(s) in a molecule has at least one lone electron pair, the molecule will be polar.

NH_3 is polar, and so is O_3

b) If the molecule contains only nonpolar bonds and there are no lone pairs on the central atom(s), the molecule will be nonpolar.

All C_xH_y molecules are nonpolar

c) If all of the atoms attached to the central atom are of the same element and there are no lone pairs on the central atom, the molecule is nonpolar.

CCl_4 and CO_2 are nonpolar

d) If the atoms attached to the central atom are of different elements, the molecule is polar.

CH_2Cl_2 and OCS are polar

e) If a molecule of a compound contains at least one N, O, F, or Cl atom, the molecule is usually polar, unless c) is true.

CH_3CH_2OH, HF, CH_3NH_2, and CH_3Cl are all polar

f) When molecules get large enough, they might have polar sections and nonpolar sections. A general rule of thumb for carbon-containing compounds is that molecules with 4/5 or fewer C atoms per polar bond can be considered to act as if they are polar. Thus, molecules with 4/5 or more C atoms per polar bond can be considered to act as if they were nonpolar.

CH_3CH_2OH is considered polar; $CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ is considered nonpolar; $CH_3CH_2CH_2CH_2OH$ is right on the polar/nonpolar divide

g) All single atoms are nonpolar. Most, but not all, molecules of elements are nonpolar.

Polar molecules have a dipole moment greater than zero, and thus are considered dipoles.

What is an Intermolecular Force?

If you have a collection of independent atoms, molecules, or ions, these particles will always exert forces of attraction and repulsion among themselves as they more closely approach each other. The repulsive forces tend to be ignored, but they do exist and come about mainly because of the repulsion of the negatively-charged electron clouds surrounding each particle (even for cations, although the positive charges do lead to repulsion with other cations and the nucleus of other atoms.)

A great deal of time is spent studying the attractive forces among independent particles. These forces are what enable molecules and atoms to gather together and remain in a condensed phase as liquids and solids. Collectively, these attractive forces are commonly known as intermolecular forces (IMFs). They are the forces of electrostatic attraction that exist between separate particles.

How is an IMF different from a bond?

Along with the common definition that bonds occur **within** molecules and IMFs occur **between** molecules, there are two closely related factors that distinguish bonds and IMFs:

a. The atomic nuclei are closer together in a bond between two atoms than in an IMF between two particles.

b. The potential energy released when a bond forms is greater than the potential energy released when an IMF forms.

These statements are generalizations, and there are certainly exceptions, but they hold true for most common substances.

What are the Types of IMFs?

The simplest way to categorize IMFs is to classify the particles that are interacting as one of the following:

a. ions
b. polar molecules
c. nonpolar molecules

From these three particle types, you can describe five different types of interparticle interactions:

1. dipole/dipole forces
2. **ion/dipole** forces
3. **dipole/induced dipole** forces.
4. **ion/induced dipole** forces
5. **dispersion** or **London** forces

(All particles exert and experience London forces, but the **<u>only</u>** forces among nonpolar particles are London forces)

The only remaining interaction would be ions interacting with ions, but that is an ionic bond. There is, however, a sixth IMF. It is a case of extreme dipole/dipole interactions:

6. molecules with very polar bonds interacting with molecules with very polar bonds – known as **hydrogen bonding** (but it is NOT a bond!)

    The only bonds that are polar enough to result in a large enough partial positive charge on a small atom are:

$$\delta^- \ \delta^+ \ \delta^- \ \delta^+ \ \delta^- \ \delta^+$$

F—H, O—H, and N—H bonds.

The only atoms that have a large enough EN value to result in a large enough partial negative charge on a small atom are:

$$\delta^- \ \delta^- \ \delta^-$$

F, O, and N

What Substances Will Mix with Each Other to Create a Solution?

> This discussion ignores entropy and focuses on enthalpy, but entropy definitely plays a role. That discussion is for later.

A solution is a homogeneous mixture in which the solute particles are so small that they cannot be filtered out and so dispersed throughout the mixture that they do not scatter a beam of light that travels through the mixture. The probability of one substance dissolving/mixing in/with another substance to form a solution depends on whether or not the newly formed IMFs are as energetically favorable as the currently existing IMFs. Thus, the mutual solubility of two substances depends mainly on the substance with the IMFs that involve the largest charge separation. In other words, there is a hierarchy of what will mix:

a) Ionically-bonded solids will form a solution (dissolve) in a solvent only if the solvent can provide very strong ion/dipole interactions.

- Usually water is the only material that can dissolve inorganic salts to any great extent, although some inorganic salts dissolve slightly in methanol and DMSO. You can find tables of solubility rules for common inorganic salts in water. One of these rules is that almost all compounds containing Group IA cations are soluble.

- Organic salts have a reasonable solubility in many polar organic solvents, but are generally much more soluble in water than in these organic solvents. The non-organic counter cations are usually Na^+, K^+, or NH_4^+, all of which generally form soluble salts. The non-organic counter anions are usually Cl^-, NO_3^-, and SO_4^{2-}, all of which generally form soluble salts.

b) Water will form a solution (mix or dissolve) with another covalently-bonded substance only if:

i) the molecules of that substance can form hydrogen bonds with the water molecules.

-The molecules of the other substance do not need to be able to form hydrogen bonds among themselves when in the pure form, but they must be polar molecules and contain an N, O, or F atom that has a partial negative charge. Acetone is an example of such a substance.

The ability of a molecule to form hydrogen bonds with water molecules does not guarantee that the molecule will dissolve in water. If there is a portion of the molecule that is nonpolar, this nonpolar section interferes with the water molecules' ability to form hydrogen bonds among themselves. Thus, the larger the nonpolar section, the less soluble the substance is in water. A general rule of thumb is the **4-5 carbon atom rule**: Molecules with fewer than 4-5 C atoms per hydrogen bonding group will likely be soluble in water. Molecules with more than 4-5 C atoms per hydrogen bonding group will likely be insoluble in water. The water solubility of molecules with 4-5 C atoms per hydrogen bonding group is best determined by experiment or by a search of the literature. For instance, the following compounds, all of which are polar and can form hydrogen bonds with water, contain four C atoms per molecule: butanoic acid is soluble with water in all ratios; 1-butanol is reasonably soluble in water; and diethyl ether is so slightly soluble in water that it is considered insoluble.

or

ii) the molecules of that substance react with water molecules to form ions, which then dissolve in the water because of ion/dipole interactions.

- The six strong acids (HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4) are the most common examples. All of these acids have K_a values greater than 10. (Remember, the K_a value tells you how likely it is for the acid to react with water, and a K_a greater than 1 means that the reaction is product-favored at equilibrium)

All molecular weak acids and molecular weak bases react with water to some extent to create ions, but these weak acids all have K_a values that are less than 1 and these weak bases all have K_b values that are less than 1. Thus, all these reactions are considered reactant-favored, and for purposes of predicting water solubility, we ignore the fact that some ions are formed. Remember that the intact weak acid or weak base molecules may themselves dissolve in water through hydrogen bonding. (See section b) (i) above.

c) The common adage "Like dissolves like" works well for most **organic** compounds. Polar compounds tend to mix well with other polar compounds. The IMFs involved can be hydrogen boding, dipole/dipole, and London forces. Nonpolar compounds tend to mix well with other nonpolar compounds, with London forces being the only IMF involved.

- With a few notable exceptions (CCl_4, for instance), organic compounds containing chlorine and bromine and iodine do have a dipole moment, and are therefore polar molecules. These molecules cannot, however, form hydrogen bonds with water, nor are the halogen atoms present as ions. Thus, halogenated organic compounds do not dissolve well in water.
- Because most organic compounds have at least one small nonpolar section on their molecules, some polar organic compounds mix well with nonpolar organic compounds.

d) Solubility in aqueous acid solutions and/or aqueous base solutions is a confusing concept, mainly because of the way that chemists talk about the process. The statement, "Check the solubility of benzoic acid in 3 M NaOH" may be clear to a practicing chemist, but it is misleading to most beginning students. The statement would be much clearer if it were written, "Check the water solubility of the organic anion formed when benzoic acid reacts with the OH^- ion in an aqueous 3M NaOH solution." The same clarity, or lack thereof, is true for statements about solubility in aqueous acid solutions.

The order of events when an aqueous solution of a base is added to an organic compound that can act as an acid is:

i) The organic compound reacts with the OH^- ion, donating an H^+ ion to the OH^- ion.

ii) The products of this reaction are water and the conjugate base of the organic compound. If the original organic compound was a neutral molecule, the conjugate base will be a water-soluble anion.

The order of events when an aqueous solution of an acid is added to an organic compound that can act as a base is:

i) The organic compound reacts with the acid, accepting an H^+ ion.

ii) The products of this reaction are the conjugate base of the acid, and the conjugate acid of the organic compound. If the original organic compound was a neutral molecule, the conjugate acid will be a water-soluble cation.

If no acid/base reaction occurs between the aqueous acid/base and the organic compound, then the organic compound remains as a neutral substance, and maintains its original solubility (or lack thereof) in water.

> **If knowing the solubility of two compounds is an essential piece of information for your work, it is always best to not only look up the solubility data, but also perform careful solubility tests yourself in the lab.**

4.10 Factors Affecting Solubility

Skills to Develop

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure 1 shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and CH_3CO_2Na) exhibit a dramatic increase in solubility with increasing temperature. Others (such as $NaCl$ and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

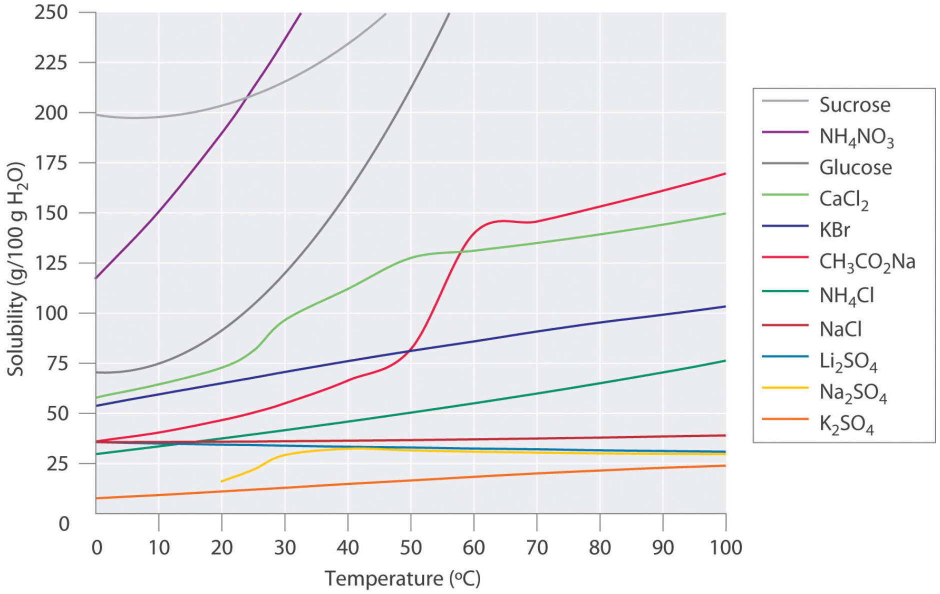


Figure 1: *Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.*

Notice in particular the curves for NH_4NO_3 and $CaCl_2$. The dissolution of ammonium nitrate in water is endothermic ($\Delta H_{soln} = +25.7\ kJ/mol$), whereas the dissolution of calcium chloride is exothermic ($\Delta H_{soln} = -68.2\ kJ/mol$), yet Figure 1 shows that the solubility of both compounds increases sharply with increasing temperature. In fact, the magnitudes of the changes in both enthalpy and entropy for dissolution are temperature dependent. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallization, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 1, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g − 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 1 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be more soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{soln} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas. The phenomenon is similar to that involved in the increase in vapor pressure of a pure liquid with increasing temperature. In the case of vapor pressure, however, it is attractive forces between solvent molecules that are being overcome by the added thermal energy when the temperature is increased.

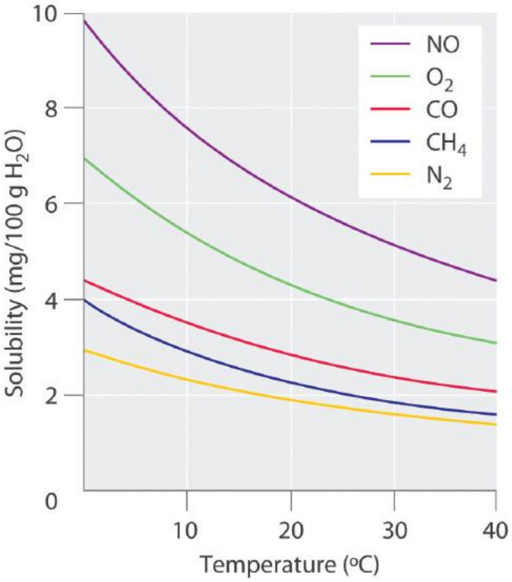


***Figure 2:** Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm. The solubilities of all gases decrease with increasing temperature.*

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called “boiler scale,” a deposit that can seriously decrease the capacity of hot water pipes (Figure 3). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex and will be described elsewhere, but the driving force is the loss of dissolved CO_2 from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate ($Ca(HCO_3)_2$ is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$2HCO^-_{3(aq)} \rightarrow CO^{2-}_{3(aq)} + H_2O_{(l)} + CO_{2(aq)} \tag{13.9}$$

Heating the solution decreases the solubility of CO_2, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.

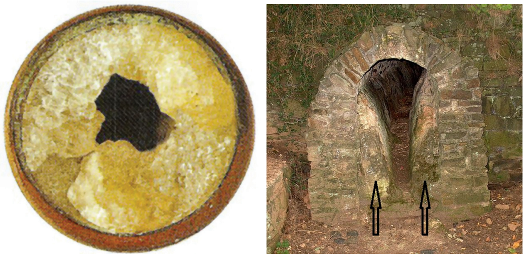


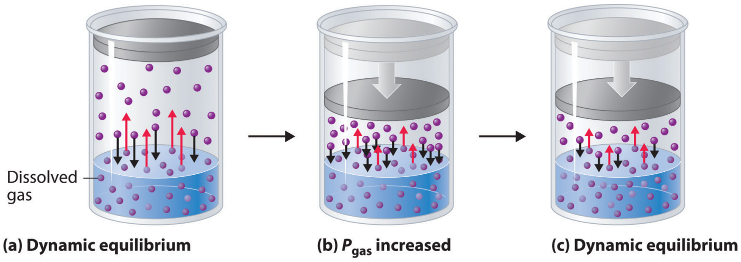
Figure 3: *Calcium carbonate deposits (left) Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures. (right) Highly calcified remains of Eiffel aqueduct near Euskirchen-Kreuzweingarten, Germany. Figure used with permission from Wikipedia*

In thermal pollution, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 2), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.

A similar effect is seen in the rising temperatures of bodies of water such as the Chesapeake Bay, the largest estuary in North America, where global warming has been implicated as the cause. For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelsgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 4, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.



(a) Dynamic equilibrium **(b) P_{gas} increased** **(c) Dynamic equilibrium**

Figure 4: *A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface*

of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP \tag{13.3.1}$$

where

- C is the concentration of dissolved gas at equilibrium,
- P is the partial pressure of the gas, and
- k is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 1.

As the data in Table 1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2. Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2, which explains its high solubility.

Table* 1*: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+_{(aq)}$ and $Cl^-_{(aq)}$, not dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

> *Gases that react with water do not obey Henry's law.*

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin.

Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these “blood substitutes” do not require refrigeration and have a long shelf life. Their very high Henry’s law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry’s law describes the relationship between the pressure and the solubility of a gas.

- Modified by Tom Neils (Grand Rapids Community College)

4.11 Suspensions and Colloids

Skills to Develop

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of homogeneous and heterogeneous mixtures. A suspension is a mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions.

Deciding whether to categorize the colloid or suspension as a homogeneous or heterogeneous mixture is a challenge. If "homogeneous" is defined to mean that the mixture is uniform in concentration and appearance throughout the entire mixture, then most colloids and **well-mixed** suspensions are homogeneous. Examples would be fog and milk (colloids); and freshly stirred paint and hot chocolate (suspensions). If you let a suspension sit for long enough, however, the particles will settle out, leaving you with a heterogeneous mixture.

Table* 1*: *Properties of Liquid Solutions, Colloids, and Suspensions*

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham’s law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning “glue”) to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun’s light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 1.

Figure* 1*: *Tyndall Effect, the Scattering of Light by Colloids*

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

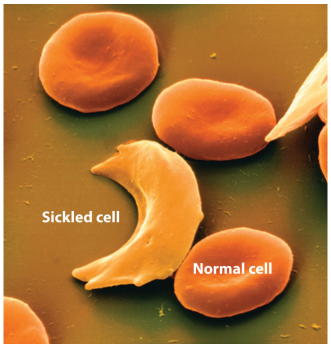


Figure* 2*: *Sickle-Cell Anemia The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.*

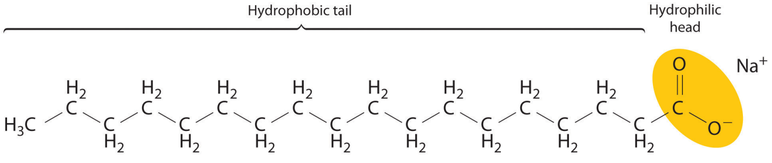
In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

Figure 3: *Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).*

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 3. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

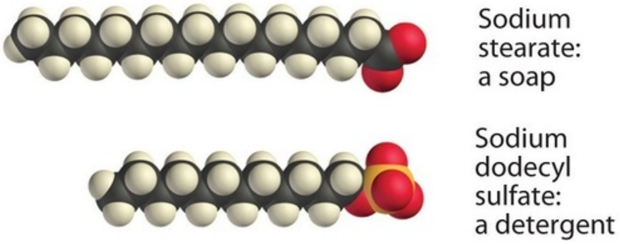
Emulsions

Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic "tail" with a hydrophilic "head":



Sodium stearate: a soap

Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate $[CH_3(CH_2)_{16}CO_2-Na^+]$, and detergents, such as sodium dodecyl sulfate $[CH_3(CH_2)_{11}OSO_3-Na^+]$, whose structures are as follows:



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called bile into the small intestine. Bile contains a variety of bile salts, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (Figure $4a$).

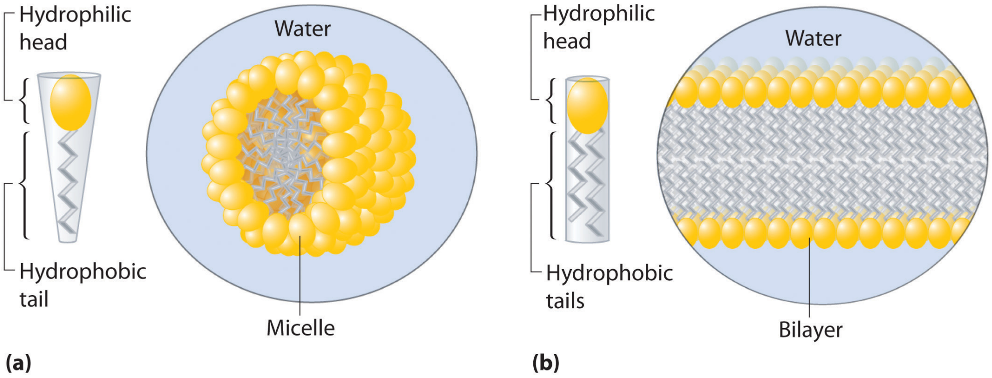
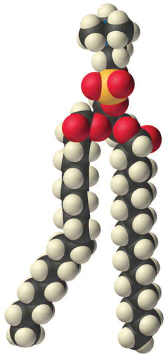


Figure 4: *Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.*

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in Figure $4b$, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



Phosphatidylcholine:
a phospholipid

A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

4.12 Practice Problems

Intermolecular Forces

CHAPTER OVERVIEW

5: The Numbers Game - Solutions and Stoichiometry

5.1 Expressing Solution Concentration

Skills to Develop

- To describe the concentrations of solutions quantitatively
- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.
- To be familiar with the different units used to express the concentrations of a solution.

Many people have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the concentration of a solution is the quantity of a **solute** that is contained in a particular quantity of **solvent** or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for solution reactions. Chemists use many different methods to define concentrations, some of which are described in this section.

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is defined as the number of moles of solute present in exactly 1 L of solution. It is, equivalently, the number of millimoles of solute present in exactly 1 mL of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{1}$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the molar concentration of a solute. Therefore,

$$[\text{sucrose}] = 1.00\text{ M} \tag{2}$$

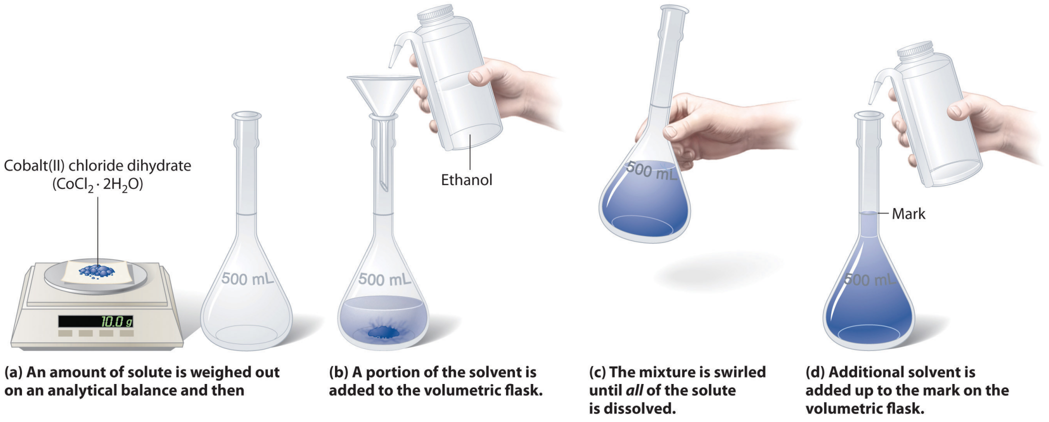
is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

$$V_L\ x\ M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{3}$$

or

$$V_{mL}\ x\ M_{mmol/mL} = \cancel{mL}\left(\frac{mmol}{\cancel{mL}}\right) = mmoles \tag{4}$$

Figure 1 illustrates the use of Equations 3 and 4.



(a) An amount of solute is weighed out on an analytical balance and then
(b) A portion of the solvent is added to the volumetric flask.
(c) The mixture is swirled until *all* of the solute is dissolved.
(d) Additional solvent is added up to the mark on the volumetric flask.

***Figure 1**: Preparation of a Solution of Known Concentration Using a Solid Solute*

Example 1: Calculating Moles from Concentration of NaOH

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use either Equation 3 or Equation 4, depending on the units given in the problem.

Solution:

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation 3 is more useful:

$$moles\ NaOH = V_L\ x\ M_{mol/L} = (2.50\ \cancel{L})\left(\frac{0.100\ mol}{\cancel{L}}\right) = 0.250\ mol\ NaOH$$

Exercise 1: Calculating Moles from Concentration of Alanine

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer

41.6 mmol

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 1 illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure 2, for some substances this effect can be significant, especially for concentrated solutions.

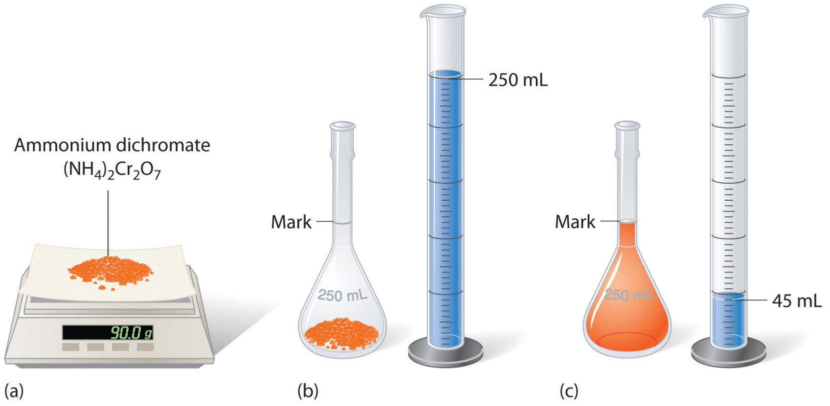


***Figure 2**: Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water. The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.*

Example 2

The solution contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2•2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2 \bullet 2\,H_2O$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $\mathrm{CoCl_2 \bullet 2\,H_2O}$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $CoCl_2$•$2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left(\frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol} \right) = 0.0603\ mol$$

The volume of the solution in liters is

$$volume = 500\ \cancel{mL} \left(\frac{1\ L}{1000\ \cancel{mL}} \right) = 0.500\ L$$

Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O$$

Exercise 2

The solution shown in Figure 2 contains 90.0 g of $(NH_4)_2Cr_2O_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer

$$(NH_4)_2Cr_2O_7 = 1.43\ M$$

To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 3. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 3.

Example 3: D5W Solution

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

A. Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.
B. Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:

$$V_L M_{mol/L} = moles$$

$$500\ \cancel{mL} \left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}} \right) \left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}} \right) = 0.155\ mol\ glucose$$

B We then convert the number of moles of glucose to the required mass of glucose:

$$mass\ of\ glucose = 0.155\ \ mol\ \cancel{glucose} \left(\frac{180.16\ g\ glucose}{1\ \ mol\ \cancel{glucose}} \right) = 27.9\ g\ glucose$$

Exercise 3

Another solution commonly used for intravenous injections is normal saline, a 0.16 M solution of sodium chloride in water. Calculate the mass of sodium chloride needed to prepare 250 mL of normal saline solution.

Answer

2.3 g NaCl

Dilution

A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in Figure 3. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

$$(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d) \tag{5}$$

where the subscripts *s* and *d* indicate the concentrated stock solution and the desired dilute solution, respectively. Example 4 demonstrates the calculations involved in diluting a concentrated stock solution.

(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration.

(b) The measured volume of stock solution is transferred to a second volumetric flask.

(c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

Figure 3: *Preparation of a Solution of Known Concentration by Diluting a Stock Solution. (a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [(V_s)(M_s) = (V_d)(M_d)].*

Example 4

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 3?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A. Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.
B. To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4.5.3 was 0.310 M glucose. We begin by using Equation 4.5.4 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$moles\ glucose = 2500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.310\ mol\ glucose}{1\ \cancel{L}}\right) = 0.775\ mol\ glucose \tag{6}$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$volume\ of\ stock\ soln = 0.775\ \cancel{mol\ glucose}\left(\frac{1\ L}{3.00\ \cancel{mol\ glucose}}\right) = 0.258\ L\ or\ 258\ mL \tag{7}$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.5.4 for V_s and substituting the appropriate values:

$$V_s = \frac{(V_d)(M_d)}{M_s} = \frac{(2.500\ L)(0.310\ \cancel{M})}{3.00\ \cancel{M}} = 0.258\ L \tag{8}$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise 4

What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

Answer

16 mL

Ion Concentrations in Solution

In Example 2, the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL were calculated to be 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion per formula unit. Like other many ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $Cr_2O_7^{2-}$ ions:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \tag{9}$$

Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure 4).

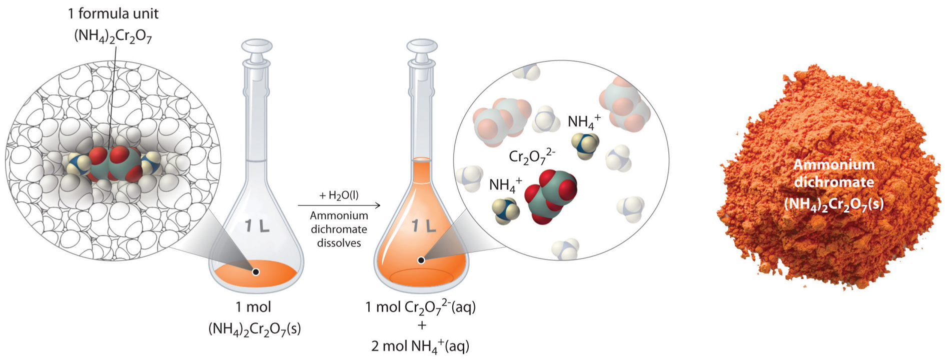


Figure 4: *Dissolution of 1 mol of an Ionic Compound. In this case, dissolving 1 mol of* $(NH_4)_2Cr_2O_7$ *produces a solution that contains 1 mol of* $Cr_2O_7^{2-}$ *ions and 2 mol of* NH_4^+ *ions. (Water molecules are omitted from a molecular view of the solution for clarity.)*

When carrying out a chemical reaction using a solution of a salt such as ammonium dichromate, it is important to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(NH_4)_2Cr_2O_7$, then the concentration of $Cr_2O_7^{2-}$ must also be 1.43 M because there is one $Cr_2O_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is 2 × 1.43 M = 2.86 M. Because each formula unit of $(NH_4)_2Cr_2O_7$ produces *three* ions when dissolved in water ($2NH_4^+ + 1Cr_2O_7^{2-}$), the *total* concentration of ions in the solution is 3 × 1.43 M = 4.29 M.

Example 5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.21 M NaOH
b. 3.7 M $(CH_3)_2CHOH$
c. 0.032 M $In(NO_3)_3$

Given: molarity

Asked for: concentrations

Strategy:

A Classify each compound as either a strong electrolyte or a nonelectrolyte.

B If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

Solution:

1. Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution:

   $$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

   B Because each formula unit of NaOH produces one Na^+ ion and one OH^- ion, the concentration of each ion is the same as the concentration of NaOH: $[Na^+]$ = 0.21 M and $[OH^-]$ = 0.21 M.

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –OH group, so it is an alcohol. Recall from Section 4.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

   B The only solute species in solution is therefore $(CH_3)_2CHOH$ molecules, so $[(CH_3)_2CHOH]$ = 3.7 M.

3. **A** Indium nitrate is an ionic compound that contains In^{3+} ions and NO_3^- ions, so we expect it to behave like a strong electrolyte in aqueous solution:

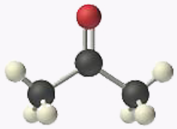
   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

B One formula unit of $In(NO_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M In^{3+} and 3 × 0.032 M = 0.096 M NO_3^-—that is, $[In^{3+}]$ = 0.032 M and $[NO_3^-]$ = 0.096 M.

Exercise 5

What are the concentrations of all species derived from the solutes in these aqueous solutions?

a. 0.0012 M $Ba(OH)_2$
b. 0.17 M Na_2SO_4
c. 0.50 M $(CH_3)_2CO$, commonly known as acetone



Acetone
$(CH_3)_2CO$

Answer a

$$[Ba^{2+}] = 0.0012\ M;\ [OH^-] = 0.0024\ M$$

Answer b

$$[Na^+] = 0.34\ M;\ [SO_4^{2-}] = 0.17\ M$$

Answer c

$$[(CH_3)_2CO] = 0.50\ M$$

Other Concentration Units

There are several different ways to quantitatively describe the concentration of a solution. For example, **mole fraction,** $\frac{moles\ solute}{total\ moles\ of\ all\ components}$, is used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 6 shows the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 6: Molarity and Mole Fraction

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A. Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.
B. Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

A The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass. The volume of the solution equals its mass divided by its density. The calculations follow:

$$\text{moles } CH_3CO_2H = \frac{3.78\ \cancel{g}\ CH_3CO_2H}{60.05\ \cancel{g}/mol} = 0.0629\ mol$$

$$\text{volume} = \frac{\text{mass}}{\text{density}} = \frac{100.0\ \cancel{g}\ \text{solution}}{1.00\ \cancel{g}/mL} = 100\ mL$$

$$\begin{aligned}\text{molarity of } \mathrm{CH_3CO_2H} &= \frac{\text{moles } \mathrm{CH_3CO_2H}}{\text{liter solution}}\\ &= \frac{0.0629\ mol\ \mathrm{CH_3CO_2H}}{(100\ \cancel{mL})(1\ L/1000\ \cancel{mL})} = 0.629\ M\ \mathrm{CH_3CO_2H}\end{aligned}$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than $\frac{1}{2}$ mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

B To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g − 3.78 g) = 96.2 g of water. We have

$$moles\ \mathrm{H_2O} = \frac{96.2\ \cancel{g}\ \mathrm{H_2O}}{18.02\ \cancel{g}/mol} = 5.34\ mol\ \mathrm{H_2O}$$

The mole fraction χ of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$\begin{aligned}\chi_{\mathrm{CH_3CO_2H}} &= \frac{moles\ \mathrm{CH_3CO_2H}}{moles\ \mathrm{CH_3CO_2H} + moles\ \mathrm{H_2O}}\\ &= \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol}\\ &= 0.0116 = 1.16 \times 10^{-2}\end{aligned}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

Exercise 6: Molarity and Mole Fraction

A solution of HCl gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of HCl per 100.0 g of solution, and its density is 1.10 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Answer a

6.10 M HCl

Answer b

$\chi_{HCl} = 0.111$

The concentration of a solution can also be described by its **molality** (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{10}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as **percent by mass**, **parts per million** (ppm), or **parts per billion** (ppb):

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{11}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{12}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{13}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

Example 7: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned} \text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63 \times 10^{-4} M \end{aligned}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$\begin{aligned} \text{mass of benzene} &= \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}} \\ &= 3.18\ mg \\ &= 3.18 \times 10^{-3}\ g\ \text{benzene} \end{aligned}$$

Exercise 7: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a

4.3×10^{-8} M

Answer b

2×10^{-6} g

Concentrations are also often reported on a **mass-to-volume** (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/v basis is the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/v. Even though reported on a mass-to-volume basis, the concentrations of very dilute solutions are often expressed in *parts per million* (*ppm*) or in *parts per billion* (*ppb*). For aqueous solutions at 20°C, 1 ppm corresponds to 1 μg per milliliter, and 1 ppb corresponds to 1 ng per milliliter.

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 1 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 8.

***Table 1**: Different Units for Expressing the Concentrations of Solutions**

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
percent by mass (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Unit	Definition	Application
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Example 8: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as “80 proof,” which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the percent by mass
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: percent by mass, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the percent by mass of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL})\left(\frac{0.789\ g}{\cancel{mL}}\right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The percent by mass of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned}\%EtOH &= \left(\frac{mass\ of\ EtOH}{mass\ of\ solution}\right)(100) \\ &= \left(\frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O}\right)(100) \\ &= 34.5\%\end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$moles\ \mathrm{CH_3CH_2OH} = (31.6\ \ g\ \cancel{\mathrm{CH_3CH_2OH}})\left(\frac{1\ mol}{46.07\ \ g\ \cancel{\mathrm{CH_3CH_2OH}}}\right)$$

$$= 0.686\ mol\ \mathrm{CH_3CH_2OH}$$

Similarly, the number of moles of water is

$$moles\ \mathrm{H_2O} = (60.0\ \ g\ \cancel{\mathrm{H_2O}})\left(\frac{1\ mol\ \mathrm{H_2O}}{18.02\ \ g\ \cancel{\mathrm{H_2O}}}\right) = 3.33\ mol\ \mathrm{H_2O}$$

The mole fraction of ethanol is thus

$$\chi_{\mathrm{CH_3CH_2OH}} = \frac{0.686\ \ \cancel{mol}}{0.686\ \ \cancel{mol} + 3.33\ \ \cancel{mol}} = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{\mathrm{CH_3CH_2OH}} = \left(\frac{0.686\ mol}{100\ \ \cancel{mL}}\right)\left(\frac{1000\ \ \cancel{mL}}{L}\right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{\mathrm{CH_3CH_2OH}} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \ \cancel{g}}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

Exercise 8: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. percent by mass
b. mole fraction
c. molarity
d. molality

Answer a

percent by mass toluene = 24.8%

Answer b

$\chi_{toluene} = 0.219$

Answer c

2.35 M toluene

Answer d

3.59 m toluene

Summary

The **concentration** of a substance is the quantity of solute present in a given quantity of solution.

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: **molarity**, moles of solute per liter of solution; **mole fraction**, the ratio of the number of moles of solute to the total number of moles of substances present; **percent by mass**, the ratio of the mass of the solute to the mass of the solution times 100; **parts per thousand** (ppt), grams of solute per kilogram of solution; **parts per million** (ppm), milligrams of solute per kilogram of solution; **parts per billion** (ppb), micrograms of solute per kilogram of solution; and **molality** (m), the number of moles of solute per kilogram of solvent.

Solution concentrations are typically expressed in terms of **molarity** and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

- **definition of molarity:**

$$molarity = \frac{moles\: of\: solute}{liters\: of\: solution} = \frac{mmoles\: of\: solute}{milliliters\: of\: solution} \tag{14}$$

- **relationship among volume, molarity, and moles**:

$$V_L\; x\; M_{mol/L} = \cancel{L} \left(\frac{mol}{\cancel{L}} \right) = moles \tag{15}$$

- **relationship between volume and concentration of stock and dilute solutions**:

$$(V_s)(M_s) = moles\: of\: solute = (V_d)(M_d) \tag{16}$$

Contributors

- Modified by Joshua Halpern (Howard University)
- Modified by Tom Neils (Grand Rapids Community College)

5.2 Types of Aqueous Solutions and Solubility

When an ionic compound dissolves in water, the positive and negative ions originally present in the crystal lattice persist in solution. Their ability to move nearly independently through the solution permits them to carry positive or negative electrical charges from one place to another. Hence the solution conducts an electrical current.

Electrolytes

Substances whose solutions conduct electricity are called electrolytes. All soluble ionic compounds are **strong electrolytes**. They conduct very well because they provide a plentiful supply of ions in solution. An example of an ionically-bonded compound that is a strong electrolyte is NaCl:

$$NaCl_{(s)} \rightarrow Na^+_{(aq)}\, Cl^-_{(aq)} \tag{1}$$

Some ionically-bonded substances behave as **weak electrolytes**—their solutions allow only a small current flow, but it is greater than that of the pure solvent. An example is mercury(II) chloride (seen in the Figure above). For a 100-*M* $HgCl_2$ solution the meter reading shows only about 0.2 percent as much current as for 0.10 *M* NaCl. When the solid dissolves only a few ions dissociate according to the equation

$$\underbrace{HgCl_2}_{99.8\%} \rightleftharpoons \underbrace{HgCl^+}_{0.2\%} + Cl^- \tag{2}$$

(The double arrows indicate that the ionization proceeds only to a limited extent and an equilibrium state is attained.)

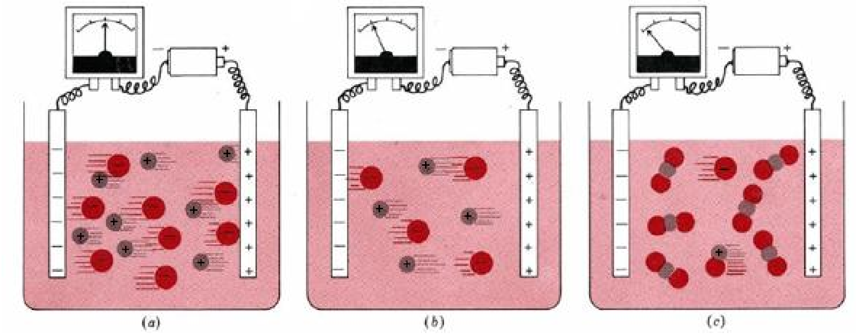


Figure* 1*: *The conductivity of electrolyte solutions: (a) 0.1 M NaCl (b) 0.05 M NaCl (c) 0.1 M* $HgCl_2$*. An electrolyte solution conducts electricity because of the movement of ions in the solution (see above). The larger the concentration of ions, the better the solutions conducts. Weak electrolytes, such as* $HgCl_2$*, conduct badly because they produce few ions when dissolved (low concentration of ions).*

The effect of the concentration of ions on the electrical current flowing through a solution is illustrated in Fig. 1. Part *a* of the figure shows what happens when a battery is connected through an electrical meter to two inert metal strips (**electrodes**) dipping in ethanol. Each cubic decimeter of such a solution contains 0.10 mol NaCl (that is, 0.10 mol Na^+ and 0.10 mol $Cl^–$). An electrical current is carried through the solution both by the Na^+ ions moving toward the negative electrode and by the Cl^- ions which are attracted toward the positive electrode. The dial on the meter indicates the quantity of current.

Figure 1*b* shows that if we replace the 0.10-*M* NaCl solution with a 0.05-*M* NaCl solution, the meter reading falls to about one-half its former value. Halving the concentration of NaCl halves the number of ions between the electrodes, and half as many ions can only carry half as much electrical charge. Therefore the current is half as great. Because it responds in such a direct way to the concentration of ions, conductivity of electrical current is a useful tool in the study of solutions.

Figure 1*c* shows that if we replace the 0.10-*M* NaCl solution with a 0.10-*M* $HgCl_2$ solution, the meter reading falls to a small fraction of its former value. Very few ions are formed in solution by the $HgCl_2$. Since only 0.2 percent of the $HgCl_2$ forms ions, the 0.10 *M* solution can conduct only about 0.2 percent as much current as 0.10 *M* NaCl.

Conductivity measurements reveal that most covalent compounds, if they dissolve in water at all, retain their original molecular structures. Neutral molecules cannot carry electrical charges through the solution, and so no current flows. A substance whose aqueous solution conducts no better than water itself is called a **nonelectrolyte**. Some examples are oxygen, O_2, ethanol, C_2H_5OH, and sugar, $C_{12}H_{22}O_{11}$. The process of the molecules dissolving intact is shown by an equation such as:

$$O_{2(g)} \rightleftharpoons O_{2(aq)} \tag{3}$$

However, some polar covalent compounds are also strong electrolytes because they react with water to form ions. Common examples are HCl, HBr, HI and H_2SO_4, all of which react with H_2O to form large concentrations of ions. For HCl, the reaction is:

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{4}$$

There are also some covalently-bonded compounds that behave as weak electrolytes. Ammonia is a common example. Only a small fraction of ammonia molecules react with water to form ions:

$$NH_{3(g)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + NH^+_{(4aq)} \tag{5}$$

Conductivity measurements can tell us more than whether a substance is a strong, a weak, or a nonelectrolyte. Consider, for instance, the data in Table 1 which shows the electrical current conducted through various aqueous solutions under identical conditions. At the rather low concentration of 0.001 *M*, the strong electrolyte solutions conduct between 2500 and 10 000 times as much current as pure H_2O and about 10 times as much as the weak electrolytes $HC_2H_3O_2$ (acetic acid) and NH_3 (ammonia).

Closer examination of the data for strong electrolytes reveals that some compounds which contain H or OH groups [such as HCl or $Ba(OH)_2$] conduct unusually well. If these compounds are excluded, we find that 1:1 electrolytes (compounds which consist of equal numbers of +1 ions and –1 ions) usually conduct about half as much current as 2:2 electrolytes (+2 and -2 ions), 1:2 electrolytes (+1 and -2 ions), or 2:1 electrolytes (+2 and -1 ions).

TABLE 1: *Electrical Current Conducted Through Various 0.001 M Aqueous Solutions at 18°C.**

Substance	***Current /mA***	**Substance**	***Current /mA***
Pure Water		**1:2 Electrolytes**	
H_2O	3.69×10^{-4}	Na_2SO_4	2.134
Weak Electrolytes		Na_2CO_3	2.24
$HC_2H_3O_2$	0.41	K_2CO_3	2.660
NH_3	0.28	**2:1 Electrolytes**	
1:1 Electrolytes		$MgCl_2$	2.128
NaCl	1.065	$CaCl_2$	2.239
NaI	1.069	$SrCl_2$	2.290
KCl	1.273	$BaCl_2$	2.312
KI	1,282	$Ba(OH)_2$	4.14
$AgNO_3$	1.131	**2:2 Electrolytes**	
HCl	3.77	$MgSO_4$	2.00
HNO_3	3.75	$CaSO_4$	2.086
NaOH	2.08	$CuSO_4$	1.97
KOH	2.34	$ZnSO_4$	1.97

* All measurements refer to a cel1 in which the distance between the electrodes is 1.0 mm and the area of each electrode is 1.0 cm^2. A potential difference of 1.0 V is applied to produce the tabulated currents.

There is a simple reason for this behavior. Under similar conditions, most ions move through water at comparable speeds. This means that ions like Mg^{2+} or SO_4^{2-}, which are doubly charged, will carry twice as much current through the solution as will singly charged ions like Na^+ or Cl^-. Consequently, a 0.001 *M* solution of a 2:2 electrolyte like $MgSO_4$ will conduct about twice as well as a 0.001 M solution of a 1:1 electrolyte like NaCl.

A similar argument applies to solutions of 1:2 and 2:1 electrolytes. A solution like 0.001 *M* Na_2SO_4 conducts about twice as well as 0.001 *M* NaCl partly because there are twice as many Na^- ions available to move when a battery is connected, but also because SO_4^{2-} ions carry twice as much charge as Cl^- ions when moving at the same speed. These differences in conductivity between different types of strong electrolytes can sometimes be very useful in deciding what ions are actually present in a given electrolyte solution as the following example makes clear.

A second, slightly more subtle, conclusion can be drawn from the data in Table 1 . When an electrolyte dissolves, each type of ion makes an independent contribution to the current the solution conducts. This can be seen by comparing NaCl with KCl, and NaI with KI. In each case the compound containing K^+ conducts about 0.2 mA more than the one containing Na^+. If we apply this observation to Na_2CO_3 and K_2CO_3, each of which produces twice as many Na^+ or K^+ ions in solution, we find that the difference in current is also twice as great—about 0.4 mA.

Thus conductivity measurements confirm our statement that each ion exhibits its own characteristic properties in aqueous solutions, independent of the presence of other ions. One such characteristic property is the quantity of electrical current that a given concentration of a certain type of ion can carry.

Example 1: Ions

At 18°C a 0.001-*M* aqueous solution of potassium hydrogen carbonate, $KHCO_3$, conducts a current of 1.10 mA in a cell of the same design as that used to obtain the data in Table 11.1. What ions are present in solution?

Solution

Referring to Table 6.2 which lists possible polyatomic ions, we can arrive at three possibilities for the ions from which $KHCO_3$ is made:

a. K^+ and H^+ and C^{4+} and three O^{2-}
b. K^+ and H^+ and CO_3^{2-}
c. K^+ and HCO_3^-

Since the current conducted by the solution falls in the range of 1.0 to 1.3 mA characteristic of 1:1 electrolytes, possibility *c* is the only reasonable choice.

Contributors

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.
- Modified by Tom Neils (Grand Rapids Community College)

5.3 Colligative Properties and Freezing Point Depression and Boiling Point Elevation and Osmosis

Skills to Develop

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol (“antifreeze”) to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin colligatus, meaning “bound together” as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind.

Vapor Pressure of Solutions and Raoult’s Law

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure 1, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

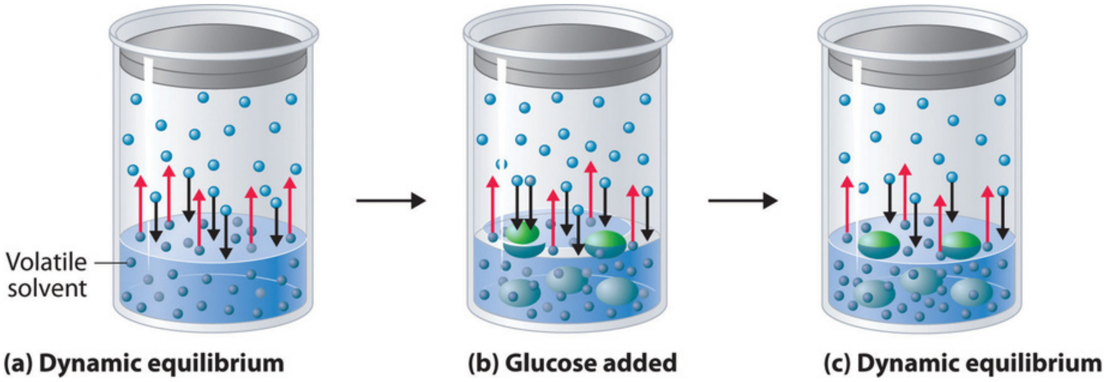


Figure* 1*: *A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water.*

Figure 2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

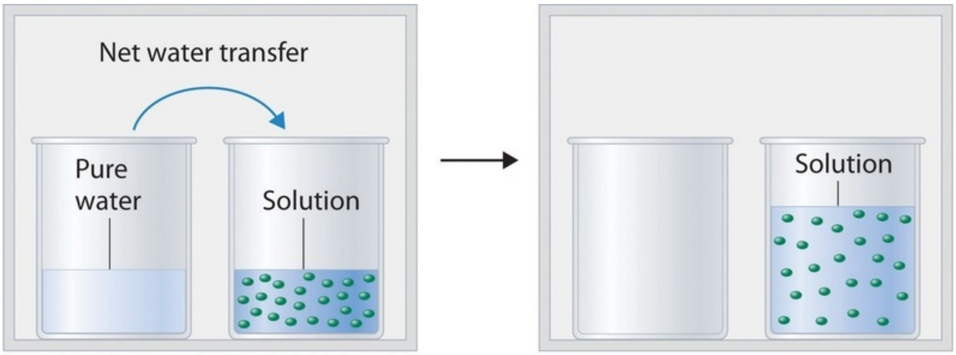


Figure* 2*: *Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution.*

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to $P = 1$ atm at a higher temperature than does the curve for pure water.

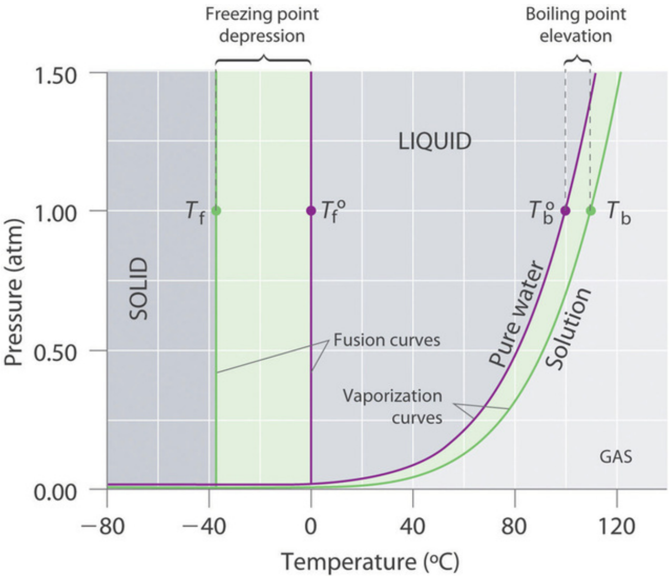


Figure 4: *Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.*

> *The boiling point of a solution with a nonvolatile solute is* ***always*** *greater than the boiling point of the pure solvent.*

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 5).

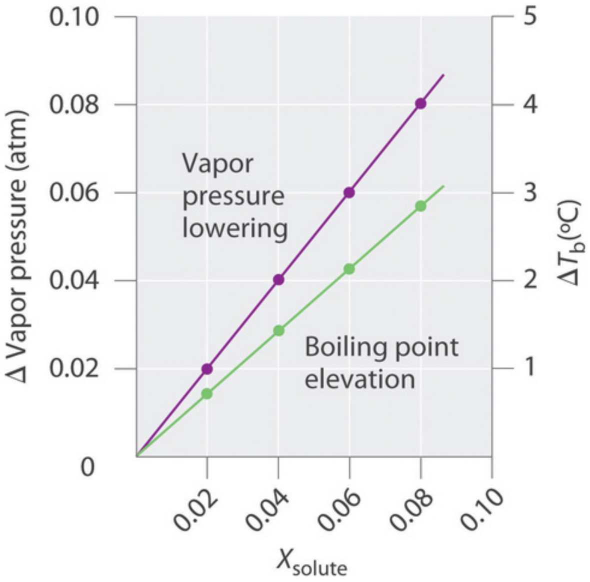


Figure 5: *Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute*

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{1}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{2}$$

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 1 lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

***Table 1**: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents*

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

Example 3

In Example 1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 2 to calculate the increase in boiling point.

Solution:

From Example 1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.98\,m$$

From Equation 2, the increase in boiling point is therefore

$$\Delta T_b = mK_b = (6.98\ \cancel{m})(0.51^\circ C/\ \cancel{m}) = 3.6^\circ C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 2 may not be valid.

Exercise 3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\, atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{3}$$

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 1 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 2:

$$\Delta T_f = mK_f \tag{4}$$

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

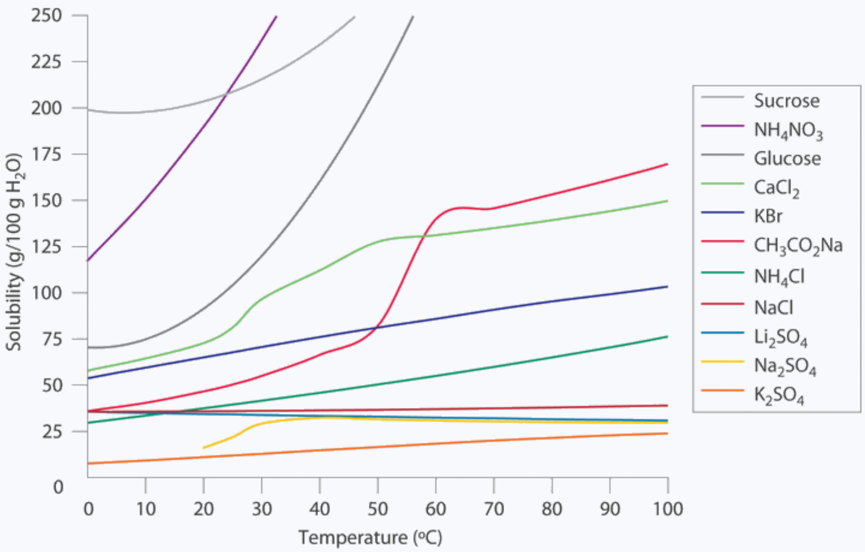
Like K_b, each solvent has a characteristic value of K_f (see Table 1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example 4: Salting the Roads

In colder regions of the United States, NaCl or $\mathrm{CaCl_2}$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of NaCl and one of $\mathrm{CaCl_2}$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.



Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.
B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 4 to calculate the freezing point depressions of the solutions.

Solution:

A From Figure above, we can estimate the solubilities of NaCl and $\mathrm{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36 \;\; g\; \cancel{NaCl}}{100 \;\; \cancel{g}\; H_2O}\right)\left(\frac{1\; mol\; NaCl}{58.44 \;\; \cancel{g\; NaCl}}\right)\left(\frac{1000 \;\; \cancel{g}}{1\; kg}\right) = 6.2\; m$$

$$m_{CaCl_2} = \left(\frac{60 \;\; g\; \cancel{CaCl_2}}{100 \;\; \cancel{g}\; H_2O}\right)\left(\frac{1\; mol\; CaCl_2}{110.98 \;\; \cancel{g\; CaCl_2}}\right)\left(\frac{1000 \;\; \cancel{g}}{1 kg}\right) = 5.4\; m$$

The lower formula mass of NaCl more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $CaCl_2$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $CaCl_2$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for NaCl and 3 × 5.4 m = 16 m for $CaCl_2$. The resulting freezing point depressions can be calculated using Equation 4:

$$NaCl : \Delta T_f = mK_f = (12 \;\; \cancel{m})(1.86^\circ C/\cancel{m}) = 22^\circ C$$

$$CaCl2 : \Delta T_f = mK_f = (16 \;\; \cancel{m})(1.86^\circ C/\cancel{m}) = 30^\circ C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $CaCl_2$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $CaCl_2$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

Exercise 4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 5 and 5.

Answer

−13.0°C

Example 5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m SrCl2, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.
B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $SrCl_2$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $SrCl_2$.

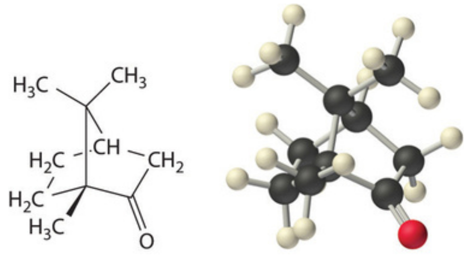
Exercise 5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m $NaCl$, 0.3 m acetic acid, 0.1 m $CaCl_2$, and 0.2 m sucrose.

Answer

0.2 m $NaCl$ (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $CaCl_2$ < 0.2 m sucrose (highest freezing point)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table 1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table 1) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

Example 6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved Sn molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 3, the measured freezing point of the solution, and the freezing point of CS_2 from Table 1 to calculate the freezing point depression. Then use Equation 4 and the value of K_f from Table 1 to calculate the molality of the solution.
B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 3:

$$\Delta T_f = T_f^0 - T_f = -112.1^\circ C - (-113.5^\circ C) = 1.4^\circ C$$

Then Equation 4 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4^\circ \cancel{C}}{3.74^\circ \cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

Exercise 6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

Answer

847 g/mol; C_{70}

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning "push"). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

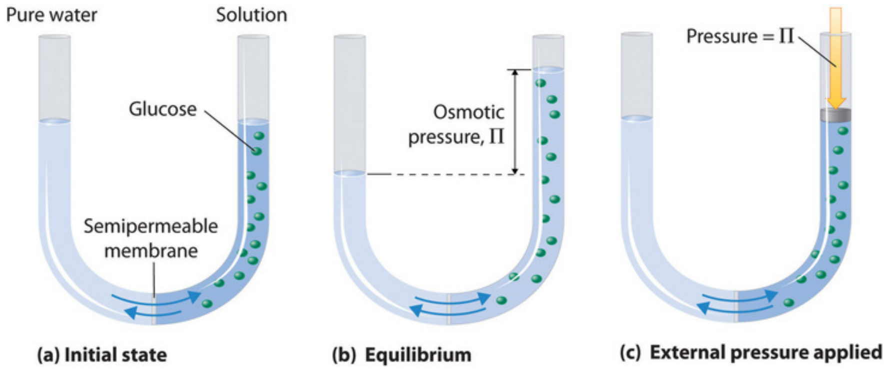


***Figure 6**: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.*

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{5}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example 7, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 5 to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 5 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$\begin{aligned} M_{NaCl} &= \frac{moles\ NaCl}{\text{liter solution}} \\ &= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ g\ \cancel{solution}}\right)\left(\frac{1.02\ \ g\ \cancel{solution}}{1.00\ \ m\cancel{L}\ solution}\right)\left(\frac{1000\ \ m\cancel{L}}{1\ L}\right) \\ &= 0.70\ M\ \text{NaCl} \end{aligned}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 5 to calculate the osmotic pressure of the solution:

$$\begin{aligned} \Pi &= MRT \\ &= (1.4\ mol/L)\left[0.0821\ (L\cdot atm)/(K\cdot mol)\right](298\ K) \\ &= 34\ atm \end{aligned}$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 5 for the molarity corresponding to this osmotic pressure:

$$\begin{aligned} M &= \frac{\Pi}{RT} \\ &= \frac{27\ \ at\cancel{m}}{[0.0821(L\cdot\ at\cancel{m})/(\ \cancel{K}\cdot mol)](298\ \ \cancel{K})} \\ &= 1.1\ M\ \text{glycerol} \end{aligned}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

Exercise 7

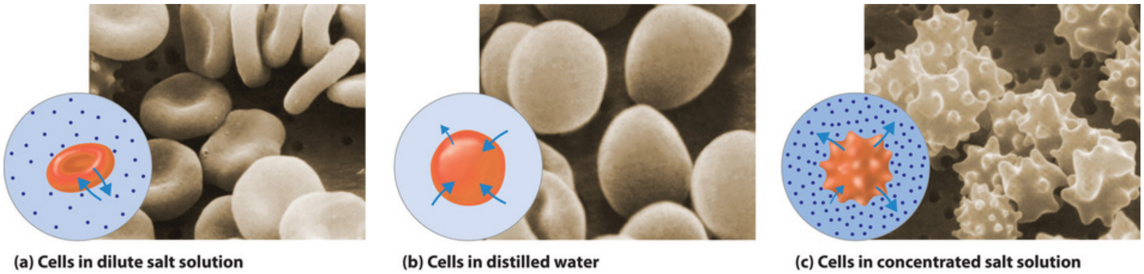
Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer

24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.


(a) Cells in dilute salt solution

(b) Cells in distilled water

(c) Cells in concentrated salt solution

Figure 7: *Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.*

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

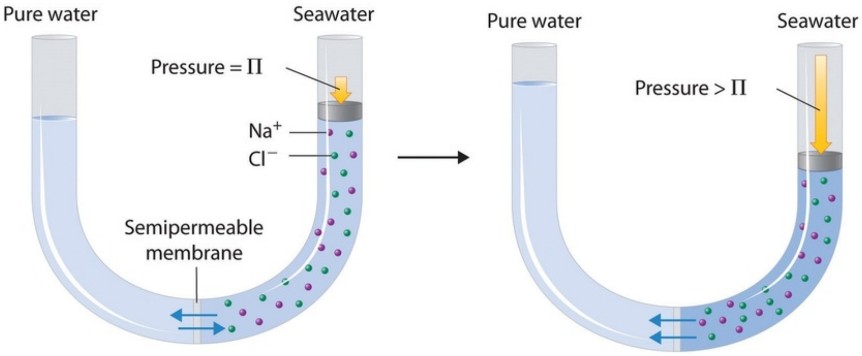


Figure 8: *Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure* (Π_{soln})*, there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In*

desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.

Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law. The boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through.

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = \chi_A P^0_A$$

- **vapor pressure lowering**:

$$P^0_A - P_A = \Delta P_A = \chi_B P^0_A$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P^0_A + (1 - \chi_A) P^0_B$$

- **boiling point elevation**:

$$\Delta T_b = mK_b i$$

- **freezing point depression:**

$$\Delta T_f = mK_f i$$

- **osmotic pressure**:

$$\Pi = nRTV = MRTi$$

- Modified by Tom Neils (Grand Rapids Community College)

5.4 Writing and Balancing Chemical Equations

Skills to Develop

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

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

Chemical Equations

As shown in Figure 1, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. This reaction is described with a chemical equation, an expression that gives the identities and quantities of the substances in a chemical reaction.

***Figure 1**: An Ammonium Dichromate Volcano: Change during a Chemical Reaction. The starting material is solid ammonium dichromate. A chemical reaction transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor (in addition, energy in the form of heat and light is released). During the reaction, the distribution of atoms changes, but the number of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced. Figure used with permission from Wikipedia. See video here:* https://www.youtube.com/watch?v=CW4hN0dYnkM

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

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \tag{1}$$

Chemical formulas and other symbols are used to indicate the starting materials, or reactants, which by convention are written on the left side of the equation, and the final compounds, or products, which are written on the right. An arrow points from the reactant to the products. The chemical reaction for the ammonium dichromate volcano in Figure 1 is

$$\underbrace{(NH_4)_2Cr_2O_7}_{reactant} \rightarrow \underbrace{Cr_2O_3 + N_2 + 4\,H_2O}_{products} \tag{2}$$

The arrow is read as “yields” or “reacts to form.” Equation 2 indicates that ammonium dichromate (the reactant) yields chromium(III) oxide, nitrogen, and water (the products). The equation for this reaction is even more informative when written as follows:

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s) + N_2(g) + 4\,H_2O(g) \tag{3}$$

Equation 3 is identical to Equation 2 except for the addition of abbreviations in parentheses to indicate the physical state of each species. The abbreviations are (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous solution, a solution of the substance in water.

Consistent with the law of conservation of mass, the numbers of each type of atom are the same on both sides of Equations 2 and 3. Each side of the reaction has two chromium atoms, seven oxygen atoms, two nitrogen atoms, and eight hydrogen atoms.

In a balanced chemical equation, both the numbers of each type of atom and the total charge are the same on both sides. Equations 2 and 3 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. A chemical reaction represents a change in the distribution of atoms, but not in the number of atoms. In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, the equation must first be balanced.

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

Balancing Simple Chemical Equations

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

$$\mathrm{C_7H_{16}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)} \tag{4}$$

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

***Figure 2**: An Example of a Combustion Reaction. The wax in a candle is a high-molecular-mass hydrocarbon, which produces gaseous carbon dioxide and water vapor in a combustion reaction (Equation 4).*

Equation 4 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, the coefficients of the reactants and products must be adjusted to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 3.

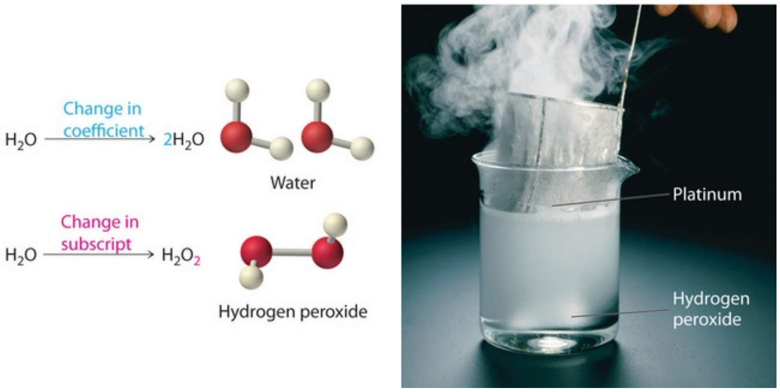


***Figure 3:** Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.*

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

Steps in Balancing a Chemical Equation

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

Example $1A$: Combustion of Heptane

To demonstrate this approach, let's use the combustion of n-heptane (Equation 4) as an example.

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

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + H_2O \tag{5}$$

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

$$C_7H_{16} + O_2 \rightarrow 7\,CO_2 + 8\,H_2O \tag{6}$$

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

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

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

Example $1B$: Combustion of Isooctane

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

$$C_8H_{18}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g) \tag{8}$$

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

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

3. **Balance polyatomic ions as a unit**. This step does not apply to this equation.

4. **Balance the remaining atoms**. Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products:

$$C_8H_{18} + O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{10}$$

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

$$C_8H_{18} + \tfrac{25}{2}O_2 \rightarrow 8\,CO_2 + 9\,H_2O \tag{11}$$

Equation 11 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{12}$$

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

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

Example 1C: Hydroxyapatite

The reaction of the mineral hydroxyapatite ($Ca_5(PO_4)_3(OH)$) with phosphoric acid and water gives $Ca(H_2PO_4)_2 \bullet H_2O$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.

Hydroxyapatite ($(Ca5(PO4)3(OH)$) *crystal*

Given: reactants and product

Asked for: balanced chemical equation

Strategy:

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

Solution:

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

$$Ca_5(PO_4)_3(OH)(s) + H_3PO_4(aq) + H_2O_{(l)} \rightarrow Ca(H_2PO_4)_2 \cdot H_2O_{(s)} \tag{13}$$

1. **B Identify the most complex substance**. We start by assuming that only one molecule or formula unit of the most complex substance, $Ca_5(PO_4)_3(OH)$, appears in the balanced chemical equation.

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

$$Ca_5(PO_4)_3(OH) + H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O \tag{14}$$

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

$$\mathrm{Ca_5(PO_4)_3(OH) + 7\,H_3PO_4 + H_2O \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O} \tag{15}$$

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

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

$$\mathrm{Ca_5(PO_4)_3(OH)(s) + 7\,H_3PO_4(aq) + 4\,H_2O(l) \rightarrow 5\,Ca(H_2PO_4)_2 \cdot H_2O(s)} \tag{16}$$

The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 41 oxygen atoms on each side.

5. **Check your work**. Both sides of the equation contain 5 calcium atoms, 10 phosphorus atoms, 30 hydrogen atoms, and 41 oxygen atoms.

Exercise 1: Fermentation

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

Commercial use of fermentation. *(a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer

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

Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides quantitative information. Specifically, it gives the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficient of that species (e.g., the 4 preceding H_2O in Equation 2). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 4, the coefficients allow Equation 2 to be interpreted in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of Cr_2O_3, 1 mol of N_2, and 4 mol of H_2O.
- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of Cr_2O_3, 28 g of N_2, and 72 g of H_2O.
- A total of 6.022×10^{23} formula units of $(NH_4)_2Cr_2O_7$ yields 6.022×10^{23} formula units of Cr_2O_3, 6.022×10^{23} molecules of N_2, and 24.09×10^{23} molecules of H_2O.

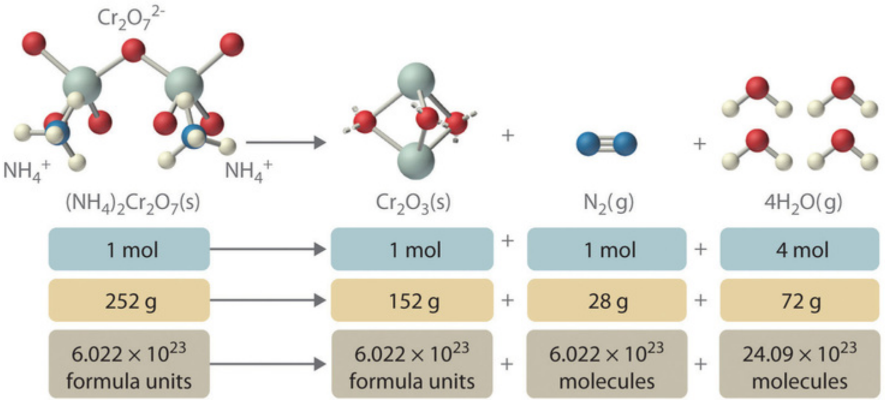


Figure 4: *The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano*

These are all chemically equivalent ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratio. For example, the mole ratio of H_2O to N_2 in Equation 2 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass:

$$252\ g \text{ of } (\mathrm{NH_4})_2\mathrm{Cr_2O_7} \tag{17}$$

yield

$$152 + 28 + 72 = 252\ g \text{ of products.} \tag{18}$$

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

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

Example 2: Combustion of Glucose

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

$$\mathrm{C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)} \tag{19}$$

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

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

d. numbers of molecules of reactants and products represented by 1 mol of glucose.

The combustion of a sugar cube consisting of sucrose with a similar reaction to the combustion of glucose. Image used with permission from Wikipedia.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

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

Solution:

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

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

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

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

$$1\,mol\,glucose\left(\frac{180.16\,g}{1\,mol\,glucose}\right) + 6\,mol\,O_2\left(\frac{31.9988\,g}{1\,mol\,O_2}\right) \tag{20}$$

$$= 6\,mol\,CO_2\left(\frac{44.010\,g}{1\,mol\,CO_2}\right) + 6\,mol\,H_2O\left(\frac{18.015\,g}{1\,mol\,H_2O}\right) \tag{21}$$

$$372.15\,g = 372.15\,g \tag{22}$$

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

In tabular form:

	$C_6H_{12}O_6\ _{(s)}$	+	$6O_2\ _{(g)}$	→	$6CO_2\ _{(g)}$		$6H_2O_{(l)}$
a.	1 molecule		6 molecules		6 molecules		6 molecules
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022×10^{23} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules		3.613×10^{24} molecule

Exercise 2: Ammonium Nitrate Explosion

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

Ammonium nitrate can be hazardous. *This aerial photograph of Texas City, Texas, shows the devastation caused by the explosion of a shipload of ammonium nitrate on April 16, 1947*. For a video click here.

The explosion resulted from the following reaction:

$$2NH_4NO_3\,_{(s)} \rightarrow 2N_2\,_{(g)} + 4H_2O_{(g)} + O_2\,_{(g)} \tag{23}$$

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

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

Answer:

	$2NH_4NO_3\,_{(s)}$	→	$2N_2\,_{(g)}$	+	$4H_2O_{(g)}$	+	$O_2\,_{(g)}$
a.	$2NH_4^+$ ions and $2NO_3^-$ ions		2 molecules		4 molecules		1 molecule
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules

Summary

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a balanced chemical equation, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

- Modified by Tom Neils (Grand Rapids Community College)

5.4a Example How Much Carbon Dioxide

Skills to Develop

- 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. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \rightarrow 8 \text{ pancakes} \tag{1}$$

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

$$24 \;\; \cancel{\text{pancakes}} \times \frac{1 \text{ egg}}{8 \;\; \cancel{\text{pancakes}}} = 3 \text{ eggs} \tag{2}$$

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:

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

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,\mathrm{NH_3}\text{ molecules}}{3\,\mathrm{H_2}\text{ molecules}} \text{ or } \frac{2\;\text{doz}\;\mathrm{NH_3}\text{ molecules}}{3\;\text{doz}\;\mathrm{H_2}\text{ molecules}} \text{ or } \frac{2\;\text{mol}\;\mathrm{NH_3}\text{ molecules}}{3\;\text{mol}\;\mathrm{H_2}\text{ molecules}} \tag{4}$$

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 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 2)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{5}$$

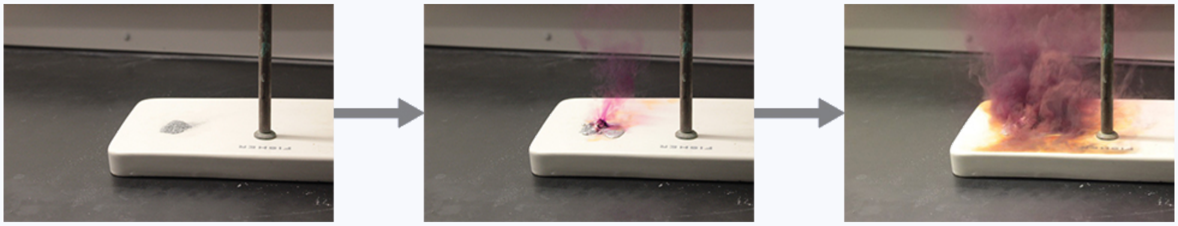
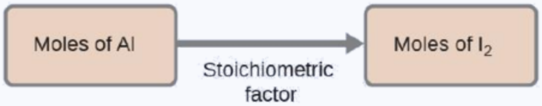


***Figure* 1**: *Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)*

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ \text{mol I}_2}{2\ \text{mol Al}}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\begin{aligned}\text{mol I}_2 &= 0.429\ \ \text{mol}\ \cancel{\text{Al}} \times \frac{3\ \text{mol I}_2}{2\ \ \text{mol}\ \cancel{\text{Al}}} \\ &= 0.644\ \text{mol I}_2\end{aligned}$$

Exercise 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 $3\,Ca(OH)_2 + 2\,H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,H_2O$?

Answer

2.04 mol

Example 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?

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{6}$$

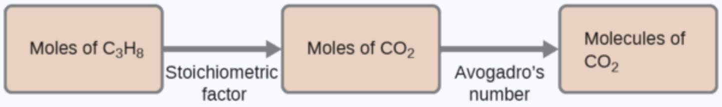
Solution

The approach here is the same as for Example 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:

$$\frac{3\ \ \text{mol CO}_2}{1\ \ \text{mol C}_3\text{H}_8} \tag{7}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ \ \text{mol}\ \cancel{\text{C}_3\text{H}_8} \times \frac{3\ \ \text{mol}\ \cancel{\text{CO}_2}}{1\ \ \text{mol}\ \cancel{\text{C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23}\ \text{CO}_2\ \text{molecules}}{\text{mol}\ \cancel{\text{CO}_2}} = 1.4 \times 10^{24}\ \text{CO}_2\ \text{molecules} \tag{8}$$

Exercise 1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O$$

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.

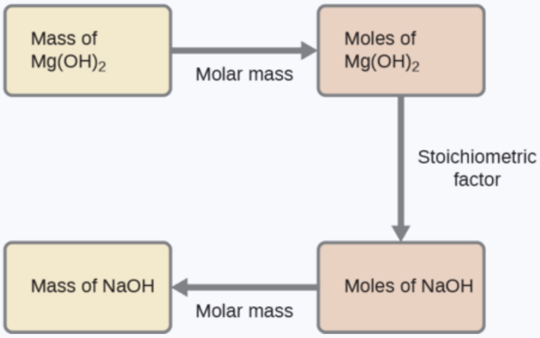
Example 3: Relating Masses of Reactants and Products

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?

$$\mathrm{MgCl_2}(aq) + 2\,\mathrm{NaOH}(aq) \rightarrow \mathrm{Mg(OH)_2}(s) + 2\,\mathrm{NaCl}(aq)$$

Solution

The approach used previously in Examples 1 and 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:



$$16\ \cancel{\text{g Mg(OH)}_2} \times \frac{1\ \cancel{\text{mol Mg(OH)}_2}}{58.3\ \cancel{\text{g Mg(OH)}_2}} \times \frac{2\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{mol Mg(OH)}_2}} \times \frac{40.0\ \text{g NaOH}}{\cancel{\text{mol NaOH}}} = 22\ \text{g NaOH} \tag{9}$$

Exercise 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 $4\,\mathrm{Ga} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{Ga_2O_3}$.

Answer

39.0 g

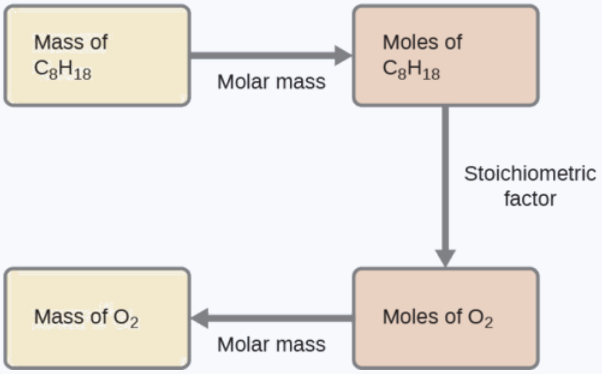
Example 4: Relating Masses of Reactants

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?

$$2\,\mathrm{C_8H_{18}} + 25\,\mathrm{O_2} \rightarrow 16\,\mathrm{CO_2} + 18\,\mathrm{H_2O}$$

Solution

The approach required here is the same as for the Example 3, differing only in that the provided and requested masses are both for reactant species.



$$702\ \text{g}\ \cancel{C_8H_{18}} \times \frac{1\ \text{mol}\ \cancel{C_8H_{18}}}{114.23\ \text{g}\ \cancel{C_8H_{18}}} \times \frac{25\ \text{mol}\ \cancel{O_2}}{2\ \text{mol}\ \cancel{C_8H_{18}}} \times \frac{32.00\ \text{g}\ O_2}{\text{mol}\ \cancel{O_2}} = 2.46 \times 10^3\ \text{g}\ O_2$$

Exercise 4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$?

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 2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

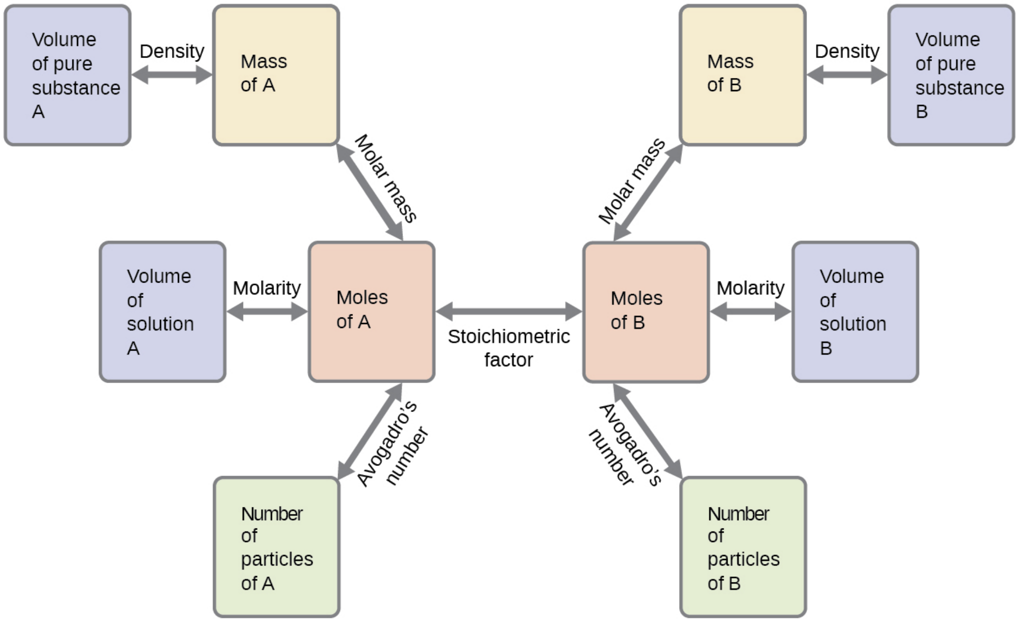


***Figure 2**: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.*

Airbags

Airbags (Figure 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:

$$2\,\mathrm{NaN_3}(s) \rightarrow 3\,\mathrm{N_2}(g) + 2\,\mathrm{Na}(s) \tag{10}$$

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 3*:* Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

Glossary

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

Contributors

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

5.5 Limiting Reactant and Theoretical Yield and Percent Yield

Skills to Develop

- To understand the concept of limiting reactants and quantify incomplete reactions

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1 \text{ box mix} + 2 \text{ eggs} \rightarrow 1 \text{ batch brownies} \tag{1}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

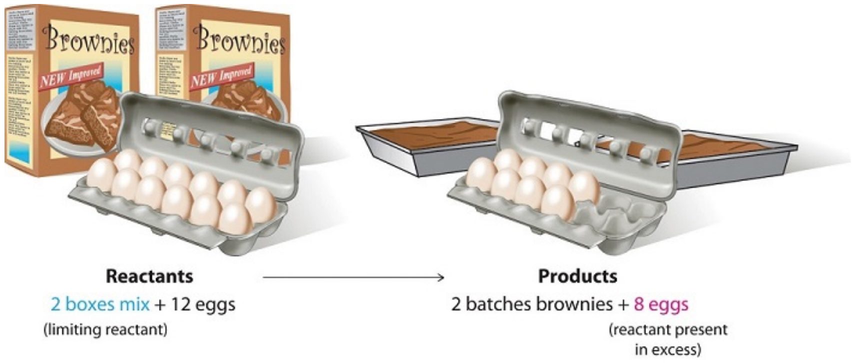


***Figure* 1**: *The Concept of a Limiting Reactant in the Preparation of Brownies*

Now consider a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth’s crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($\mathrm{TiCl_4}$) and carbon dioxide.

$$\mathrm{TiO_2(s) + Cl_2(g) \rightarrow TiCl_4(g) + CO_2(g)} \tag{2}$$

Titanium tetrachloride is then converted to metallic titanium by reaction with molten magnesium metal at high temperature:

$$\mathrm{TiCl_4(g) + 2\ Mg(l) \rightarrow Ti(s) + 2\ MgCl_2(l)} \tag{3}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances, magnesium metal is the limiting reactant in the production of metallic titanium.

Figure 2: *Medical use of titanium. Here is an example of its successful use in joint replacement implants. An A-P X-ray of a pelvis showing a total hip joint replacement. The right hip joint (on the left in the photograph) has been replaced. A metal prostheses is cemented in the top of the right femur and the head of the femur has been replaced by the rounded head of the prosthesis. Figure courtesy of NIH (NIADDK) 9AO4 (Connie Raab)*

With 1.00 kg of titanium tetrachloride and 200 g of magnesium metal, how much titanium metal can be produced according to Equation 3?

Solving this type of problem requires that you carry out the following steps

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

Step 1: To determine the number of moles of reactants present, calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$\begin{aligned} \text{moles } \mathrm{TiCl_4} &= \frac{\text{mass } \mathrm{TiCl_4}}{\text{molar mass } \mathrm{TiCl_4}} \\ &= 1000 \ \cancel{g} \ \mathrm{TiCl_4} \times \frac{1 \, mol \; TiCl_4}{189.679 \ \cancel{g} \ \mathrm{TiCl_4}} \\ &= 5.272 \, mol \ \mathrm{TiCl_4} \end{aligned} \tag{4}$$

$$\begin{aligned} \text{moles } \mathrm{Mg} &= \frac{\text{mass } \mathrm{Mg}}{\text{molar mass } \mathrm{Mg}} \\ &= 200 \ \cancel{g} \ \mathrm{Mg} \times \frac{1 \ mol \, \mathrm{Mg}}{24.305 \ \cancel{g} \ \mathrm{Mg}} \\ &= 8.23 \, \mathrm{mol \ Mg} \end{aligned} \tag{5}$$

Step 2: There are more moles of magnesium than of titanium tetrachloride, but the ratio is only the following:

$$\frac{mol \, \mathrm{Mg}}{mol \, \mathrm{TiCl_4}} = \frac{8.23 \, mol}{5.272 \, mol} = 1.56 \tag{6}$$

Because the ratio of the coefficients in the balanced chemical equation is,

$$\frac{2 \, mol \, \mathrm{Mg}}{1 \, mol \, \mathrm{TiCl_4}} = 2 \tag{7}$$

there is not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, there are 8.23 mol of Mg, so (8.23 ÷ 2) = 4.12 mol of $\mathrm{TiCl_4}$ are required for complete reaction. Because there are 5.272 mol of

$\mathrm{TiCl_4}$, titanium tetrachloride is present in excess. Conversely, 5.272 mol of $\mathrm{TiCl_4}$ requires 2 × 5.272 = 10.54 mol of Mg, but there are only 8.23 mol. Therefore, magnesium is the limiting reactant.

Step 3: Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$mol\ \mathrm{Ti} = 8.23\, mol\ \mathrm{Mg} = \frac{1\, mol\ \mathrm{Ti}}{2\, mol\ \mathrm{Mg}} = 4.12\, mol\ \mathrm{Ti} \tag{8}$$

Thus only 4.12 mol of Ti can be formed.

Step 4. To calculate the mass of titanium metal that can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$\begin{aligned} \text{moles Ti} &= \text{mass Ti} \times \text{molar mass Ti} \\ &= 4.12\, mol\ \mathrm{Ti} \times \frac{47.867\, g\ \mathrm{Ti}}{1\, mol\ \mathrm{Ti}} \\ &= 197\, g\ \mathrm{Ti} \end{aligned} \tag{9}$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of $\mathrm{TiCl_4}$ and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

$$TiCl_4: \frac{5.272\, mol\, (actual)}{1\, mol\, (stoich)} = 5.272$$

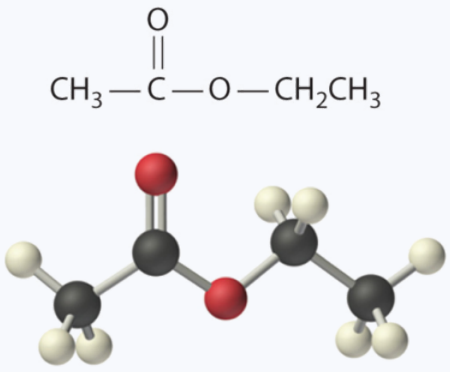
$$Mg: \frac{8.23\, mol\, (actual)}{2\, mol\, (stoich)} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 1 demonstrates.

Example 1: Fingernail Polish Remover

Ethyl acetate ($\mathrm{CH_3CO_2C_2H_5}$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol ($\mathrm{C_2H_5OH}$) with acetic acid ($\mathrm{CH_3CO_2H}$); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.



Ethyl acetate

Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A. Balance the chemical equation for the reaction.
B. Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.
C. Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.
D. Convert from moles of product to mass of product.

Solution:

A Always begin by writing the balanced chemical equation for the reaction:

$$\mathrm{C_2H_5OH(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O(l)}$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall that the density of a substance is the mass divided by the volume:

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

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

$$\begin{aligned}
\text{moles } \mathrm{C_2H_5OH} &= \frac{\text{mass } \mathrm{C_2H_5OH}}{\text{molar mass } \mathrm{C_2H_5OH}} \\
&= \frac{(\text{volume } \mathrm{C_2H_5OH}) \times (\text{density } \mathrm{C_2H_5OH})}{\text{molar mass } \mathrm{C_2H_5OH}} \\
&= 10.0\ \cancel{ml}\ \mathrm{C_2H_5OH} \times \frac{0.7893\ \cancel{g}\ \mathrm{C_2H_5OH}}{1\ \cancel{ml}\ \mathrm{C_2H_5OH}} \times \frac{1\, mol\ \mathrm{C_2H_5OH}}{46.07\ \cancel{g}\ \mathrm{C_2H_5OH}} \\
&= 0.171\, mol\ \mathrm{C_2H_5OH}
\end{aligned}$$

$$\begin{aligned}
\text{moles } \mathrm{CH_3CO_2H} &= \frac{\text{mass } \mathrm{CH_3CO_2H}}{\text{molar mass } \mathrm{CH_3CO_2H}} \\
&= \frac{(\text{volume } \mathrm{CH_3CO_2H}) \times (\text{density } \mathrm{CH_3CO_2H})}{\text{molar mass } \mathrm{CH_3CO_2H}} \\
&= 10.0\ \cancel{ml}\ \mathrm{CH_3CO_2H} \times \frac{1.0492\ \cancel{g}\ \mathrm{CH_3CO_2H}}{1\ \cancel{ml}\ \mathrm{CH_3CO_2H}} \times \frac{1\, mol\ \mathrm{CH_3CO_2H}}{60.05\ \cancel{g}\ \mathrm{CH_3CO_2H}} \\
&= 0.175\, mol\ \mathrm{CH_3CO_2H}
\end{aligned}$$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned}
moles\ \text{ethyl acetate} &= mol\ \text{ethanol} \times \frac{1\, mol\ \text{ethyl acetate}}{1\, mol\ \text{ethanol}} \\
&= 0.171\, mol\ \mathrm{C_2H_5OH} \times \frac{1\, mol\ \mathrm{CH_3CO_2C_2H_5}}{1\, mol\ \mathrm{C_2H_5OH}} \\
&= 0.171\, mol\ \mathrm{CH_3CO_2C_2H_5}
\end{aligned}$$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned}\text{mass of ethyl acetate} &= mol\ \text{ethyl acetate} \times \text{molar mass ethyl acetate} \\ &= 0.171\, mol\, \mathrm{CH_3CO_2C_2H_5} \times \frac{88.11\, g\, \mathrm{CH_3CO_2C_2H_5}}{1\, mol\, \mathrm{CH_3CO_2C_2H_5}} \\ &= 15.1\, g\, \mathrm{CH_3CO_2C_2H_5}\end{aligned}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm3) to determine the volume of ethyl acetate that could be produced:

$$\begin{aligned}\text{volume of ethyl acetate} &= 15.1\, g\, \mathrm{CH_3CO_2C_2H_5} \times \frac{1\, ml\ \mathrm{CH_3CO_2C_2H_5}}{0.9003\, g\ \mathrm{CH_3CO_2C_2H_5}} \\ &= 16.8\, ml\, \mathrm{CH_3CO_2C_2H_5}\end{aligned}$$

Exercise 1

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound P_4S_{10}. How much P_4S_{10} can be prepared starting with 10.0 g of $\mathrm{P_4}$ and 30.0 g of S_8?

Answer

35.9 g

Limiting Reactants in Solutions

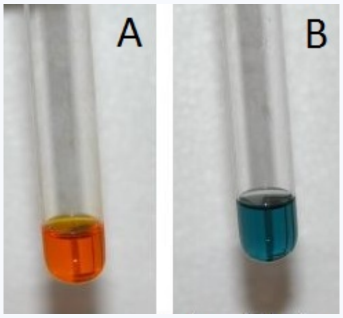
The concept of limiting reactants applies to reactions carried out in solution as well as to reactions involving pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 2.

Example 2: Breathalyzer reaction

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3\,\mathrm{CH_3CH_2OH(aq)} + \underset{yellow-orange}{2\,\mathrm{Cr_2O_7^{2-}}\,(aq)} + 16\,\mathrm{H^+(aq)} \xrightarrow[\mathrm{H_2SO_4(aq)}]{\mathrm{Ag^+}} 3\,\mathrm{CH_3CO_2H(aq)} + \underset{green}{4\,\mathrm{Cr^{3+}}}(aq) + 11\,\mathrm{H_2O(l)}$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $\mathrm{Cr_2O_7^{2-}}$ ions are reduced from $\mathrm{Cr^{6+}}$ to $\mathrm{Cr^{3+}}$. In the presence of $\mathrm{Ag^+}$ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $\mathrm{Cr_2O_7^{2-}}$ ion (the reactant) is yellow-orange and the $\mathrm{Cr^{3+}}$ ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.



A Breathalyzer reaction with a test tube before (a) and after (b) ethanol is added. When a measured volume of a suspect's breath is bubbled through the solution, the ethanol is oxidized to acetic acid, and the solution changes color from yellow-orange to green. The intensity of the green color indicates the amount of ethanol in the sample.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% H_2SO_4 as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+}?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A. Calculate the number of moles of $\mathrm{Cr_2O_7^{2-}}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.
B. Find the total number of moles of $\mathrm{Cr_2O_7^{2-}}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).
C. Use the mole ratios from the balanced chemical equation to calculate the number of moles of C_2H_5OH needed to react completely with the number of moles of $\mathrm{Cr_2O_7^{2-}}$ ions present. Then find the mass of C_2H_5OH needed by multiplying the number of moles of C_2H_5OH by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which can be used to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5\times10^{-7}\ moles$$

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $\mathrm{Cr_2O_7^{2-}}$ when it dissolves, each milliliter of solution contains 8.5×10^{-7} mol of $Cr_2O_7^{2-}$. The total number of moles of $Cr_2O_7^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5\times10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6\times10^{-6}\ mol\ Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $\mathrm{Cr_2O_7^{2-}}$ ion, so the total number of moles of C_2H_5OH required for complete reaction is

$$moles\ of\ \mathrm{C_2H_5OH} = (2.6\times10^{-6}\ \ mol\ \cancel{\mathrm{Cr_2O_7^{2-}}})\left(\frac{3\ mol\ \mathrm{C_2H_5OH}}{2\ \ mol\ \cancel{\mathrm{Cr_2O_7^{2-}}}}\right) = 3.9\times10^{-6}\ mol\ \mathrm{C_2H_5OH}$$

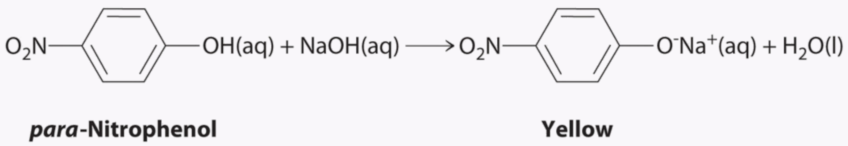
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ \mathrm{C_2H_5OH} = (3.9\times10^{-6}\ \ mol\ \cancel{\mathrm{C_2H_5OH}})\left(\frac{46.07\ g}{mol\ \cancel{\mathrm{C_2H_5OH}}}\right) = 1.8\times10^{-4}\ g\ \mathrm{C_2H_5OH}$$

Thus 1.8×10^{-4} g or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

Exercise 2

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing 7.20×10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer

4.93×10^{-5} L or 49.3 µL

In Examples 1 and 2, the identities of the limiting reactants are apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, it can be determined by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation. The only difference is that the volumes and concentrations of solutions of reactants, rather than the masses of reactants, are used to calculate the number of moles of reactants, as illustrated in Example 3.

Example 3

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

$$2\,\mathrm{AgNO_3(aq)} + \mathrm{K_2Cr_2O_7(aq)} \rightarrow \mathrm{Ag_2Cr_2O_7(s)} + 2\,\mathrm{KNO_3(aq)}$$

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $\mathrm{K_2Cr_2O_7}$ are mixed with 250 mL of 0.57 M $AgNO_3$?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A. Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.
B. Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.
C. Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

A The balanced chemical equation tells us that 2 mol of $AgNO_3$(aq) reacts with 1 mol of $K_2Cr_2O_7$(aq) to form 1 mol of $Ag_2Cr_2O_7$(s) (Figure 8.3.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

B Now determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$\mathrm{K_2Cr_2O_7}: \frac{0.085\ mol}{1\ mol} = 0.085$$

$$\mathrm{AgNO_3}: \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $\mathrm{AgNO_3}$ is the *limiting reactant*.

C Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only 0.14/2 = 0.070 mol of $Ag_2Cr_2O_7$. Finally, convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

The Ag^+ and $Cr_2O_7{}^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise 3

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2\,NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2\,CO_2(g) + Na_2SO_4(aq) + 2\,H_2O(l)$$

If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer

3.4 g

Theoretical Yields

When reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, the amount obtained if the reaction occurred perfectly and the purification method were 100% efficient.

In reality, less product is always obtained than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not run to completion, resulting in a mixture of products and reactants; this last possibility is a common occurrence. Therefore, the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$\text{percent yield} = \frac{\text{actual yield}\ \ (g)}{\text{theoretical yield}\ (g)} \times 100\% \tag{10}$$

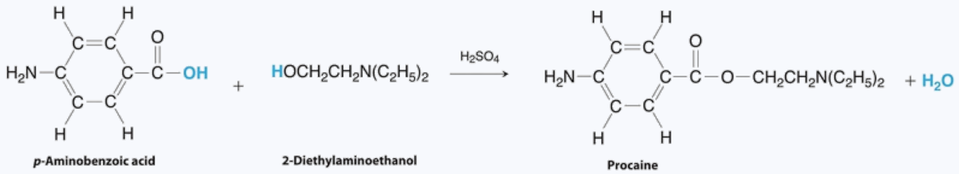
The method used to calculate the percent yield of a reaction is illustrated in Example 4.

Example 4: Novocain

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H2SO4 (indicated above the arrow) by the reaction

$$\underset{\text{p-amino benzoic acid}}{C_7H_7NO_2} + \underset{\text{2-diethylaminoethanol}}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{\text{procaine}}{C_{13}H_{20}N_2O_2} + H_2O$$

If this reaction were carried out with 10.0 g of p-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and 15.7 g of procaine were isolated, what is the percent yield?



The preparation of procaine. A reaction of p-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

Given: masses of reactants and product

Asked for: percent yield

Strategy:

A. Write the balanced chemical equation.
B. Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.
C. Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: p-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$mol \text{ p-aminobenzoic acid} = 10.0\, g \times \frac{1\, mol}{137.14\, g} = 0.0729\, mol \text{ p-aminbenzoic acid}$$

$$mol \text{ 2-diethylaminoethanol} = 10.0\, g \times \frac{1\, mol}{117.19\, g} = 0.0853\, mol \text{ 2-diethylaminoethanol}$$

The reaction requires a 1:1 mole ratio of the two reactants, so p-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of p-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula (C13H20N2O2) to calculate its molar mass, which is 236.31 g/mol.

$$\text{theoretical yield of procaine} = 0.0729\, mol \times \frac{236.31\, g}{1\, mol} = 17.2\, g$$

C The actual yield was only 15.7 g of procaine, so the percent yield (via Equation 10) is

$$\text{percent yield} = \frac{15.7\, g}{17.2\, g} \times 100 = 91.3\%$$

(If the product were pure and dry, this yield would indicate very good lab technique!)

Exercise 4: Extraction of Lead

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

$$2\,\mathrm{PbS(s)} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{PbO(s)} + 2\,\mathrm{SO_2(g)}$$

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$\mathrm{PbO(s)} + \mathrm{C(s)} \rightarrow \mathrm{Pb(l)} + \mathrm{CO(g)}$$

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?

Electrolytically refined pure (99.989 %) superficially oxidized lead nodules and a high purity (99.989 %) 1 cm^3 *lead cube for comparison.* Figure used with permission from Wikipedia.

Answer

89.2%

Percent yield can range from 0% to 100%. In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student must have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments. A 100% yield means that everything worked perfectly, and the chemist obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows the unlikelihood of a 100% yield. At the other extreme, a yield of 0% means that no product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Summary

The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained. The stoichiometry of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A stoichiometric quantity of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is in excess. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the limiting reactant. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the theoretical yield of the reaction. The actual yield is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

5.6 Representing Aqueous Reactions Molecular and Ionic and Complete Ionic Equations

Learning Objectives

- To understand what information is obtained by each type of ionic equation

The chemical equations discussed earlier showed the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

Let's consider the reaction of silver nitrate with potassium dichromate. When aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equation that shows all the reactants and products as undissociated, electrically neutral compounds:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq) \tag{1}$$

Although Equation 1 gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as $AgNO_3$ and $K_2Cr_2O_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $Ag_2Cr_2O_7$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a **complete ionic equation**, showing which ions and molecules are hydrated and which are present in other forms and phases:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq) \tag{2}$$

Note that K^+(aq) and NO_3^-(aq) ions are present on both sides of the equation, and their coefficients are the same on both sides. These ions are called **spectator ions** because they do not participate in the actual reaction. Canceling the spectator ions gives the **net ionic equation**, which shows only those species that participate in the chemical reaction:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{3}$$

Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In Equation 3, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $Ag_2Cr_2O_7$ formula unit.

By eliminating the spectator ions, we can focus on the chemistry that takes place in a solution. For example, the overall chemical equation for the reaction between silver fluoride and ammonium dichromate is as follows:

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq) \tag{4}$$

The complete ionic equation for this reaction is as follows:

$$2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq) \tag{5}$$

Because two NH_4^+(aq) and two F^-(aq) ions appear on both sides of Equation 5, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 6), which is identical to Equation 3:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) \tag{6}$$

If we look at net ionic equations, it becomes apparent that many different combinations of reactants can result in the same net chemical reaction. For example, we can predict that silver fluoride could be replaced by silver nitrate in the preceding reaction without affecting the outcome of the reaction.

Only strong electrolytes can be separated into their component ions. To determine which compounds are strong electrolytes, you first look to see if they are designated as **aqueous**, meaning their formula is followed by the symbol (aq).

Not all aqueous species can be separated into ions, be no species that are not aqueous can be separated into ions.

Once you have identified the aqueous species, you need to see if the substance is either

a) an ionically-bonded compound

or

b) one of the six strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, or H_2SO_4.

Only those aqueous compounds that fall into either category a) or b) can be separated into ions.

Thus, as you learned previously, most covalently-bonded compounds, even if tehy are aqueous, will not be separated into ions.

Example 1

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium phosphate to give solid barium phosphate and a solution of sodium nitrate.

Given: reactants and products

Asked for: overall, complete ionic, and net ionic equations

Strategy:

Write and balance the overall chemical equation. Write all the soluble reactants and products in their dissociated form to give the complete ionic equation; then cancel species that appear on both sides of the complete ionic equation to give the net ionic equation.

Solution:

From the information given, we can write the unbalanced chemical equation for the reaction:

$$Ba(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq) \tag{7}$$

Because the product is $Ba_3(PO_4)_2$, which contains three Ba^{2+} ions and two PO_4^{3-} ions per formula unit, we can balance the equation by inspection:

$$3Ba(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq) \tag{8}$$

This is the overall balanced chemical equation for the reaction, showing the reactants and products in their undissociated form. To obtain the complete ionic equation, we write each soluble reactant and product in dissociated form:

$$3Ba^{2+}(aq) + 6NO_3^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) + 6Na^+(aq) + 6NO_3^-(aq) \tag{9}$$

The six NO_3^-(aq) ions and the six Na^+(aq) ions that appear on both sides of the equation are spectator ions that can be canceled to give the net ionic equation:

$$3Ba^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) \tag{10}$$

Exercise 1

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous silver fluoride with aqueous sodium phosphate to give solid silver phosphate and a solution of sodium fluoride.

Answer:

overall chemical equation:

$$3AgF(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaF(aq) \tag{11}$$

complete ionic equation:

$$3Ag^+(aq) + 3F^-(aq) + 3Na^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) + 3Na^+(aq) + 3F^-(aq) \tag{12}$$

net ionic equation:

$$3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) \tag{13}$$

Summary

The chemical equation for a reaction in solution can be written in three ways. The **overall chemical equation** shows all the substances present in their undissociated forms; the **complete ionic equation** shows all the substances present in the form in which they actually exist in solution; and the **net ionic equation** is derived from the complete ionic equation by omitting all **spectator ions**, ions that occur on both sides of the equation with the same coefficients. Net ionic equations demonstrate that many different combinations of reactants can give the same net chemical reaction.

Key Takeaway

- A complete ionic equation consists of the net ionic equation and spectator ions.

Conceptual Problem

1. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

Contributors

- Modified by Joshua Halpern (Howard University)

5.7 Chemical Reactions and Aqueous Reactions (Exercises)

Template:HideTOC

These are homework exercises to accompany the Textmap created for Chemistry: A Molecular Approach by Nivaldo Tro. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.

Additional Questions

1. The Kingston Steam Plant burns 14,000 tons of coal each day and generates 10^{10} kilowatts-hours of electricity each year (enough for 700,000 homes). Coal is primarily carbon which undergoes combustion in the following reaction: $C(s) + O_2(g) \rightarrow CO_2(g)$

   How many grams of oxygen is required for the combustion of 1 day's coal?

   a. How much carbon dioxide is produced each day?
2. CO_2 is removed from the atomsphere by trees and converted into cellulose. The basic reaction for this is: $6\ CO_2(g) + 5\ H_2O(l) \rightarrow C_6H_{10}O_5(s) + 6\ O_2(g)$
   a. How many grams of water are required to process the CO_2 from one day's electrical production at the Kingston Steam Plant?
   b. How much oxygen is produced by this process?
   c. How much cellulose is produced?
   d. If you assume that a tree weigh's 2 tons, how many trees are required to process the CO_2 produced in one day?
3. A typical automobile gets 30 miles per gallon of gas and drives 12,000 miles every year. Assuming that octane (C_8H_{18}, density 0.7025 g cm^{-3}) is a principal component of gasoline;
   a. How much oxygen is required for a car to run for 1 year?
   b. How much CO_2 is produced by the car in 1 year?
   c. How many trees are required to remove the CO_2 produced by the car in 1 year?
4. Modern instrumental techniques are capable of detecting lead in a milliliter sample at picomolar concentration.
   a. How many moles of lead are in the sample?
   b. What is the mass of lead in this sample?
   c. How many grams of sodium chloride would be required to precipitate all the lead in this sample as lead (II) chloride?
   d. What would the mass of the lead (II) chloride precipitate be?

1.The Kingston Steam Plant burns 14,000 tons of coal each day and generates 1010 kilowatts-hours of electricity each year (enough for 700,000 homes). Coal is primarily carbon which undergoes combustion in the following reaction: C(s) + O2 (g) -> CO2 (g) a.How many grams of oxygen is required for the combustion of 1 day's coal? b.How much carbon dioxide is produced each day? Coal is the limiting reageint in this reaction (unless the earth runs out of oxygen, but then we are all in really big trouble). So first calculate the number of moles of coal. Mass coal 14000. ton Mass = coal 1.4 104 . . ton 2000. lb 1. ton 453.6.gm lb Mass = coal 1.27 1010 gm MW C 12.011.gm.mole 1 Mole C Mass coal MW C Mole = C 1.057 109 mole From the balanced reaction; for every mole of carbon, one mole of oxygen is required, and one mole of CO2 is produced. Mass of O2 Mole O2 Mole C MW O2 2.15.9994.gm.mole 1 Mass O2 Mole . O2 MW O2 Mass = O2 3.384 1010 gm Mass of CO2 Mole CO2 Mole C MW CO2 . . (12.011) 2.15.9994 gm mole 1 Mass CO2 Mole . CO2 MW CO2 Mass = CO2 4.654 1010 gm S.E. Van Bramer Widener University 11/4/97 2.CO2 is removed from the atomsphere by trees and converted into cellulose. The basic reaction for this is: 6 CO2 (g) + 5 H2O (l) -> C6H10O5 (s) + 6 O2 (g) a.How many grams of water are required to process the CO2 from one day's electrical production at the Kingston Steam Plant? b.How much oxygen is produced by this process? c.How much cellulose is produced? d.If you assume that a tree weigh's 2 tons, how many trees are required to process the CO2 produced in one day? From the balanced chemical reaction, five moles of water are required for 6 moles of carbon dioxide: Mole H2O Mole . CO2 5 6 Mole = H2O 8.812 108 mole MW H2O . . ( ) 2.1.00794 15.9994 gm mole 1 Mass H2O Mole . H2O MW H2O Mass = H2O 1.587 1010 gm Density H2O 1. gm mL Volume H2O Mass H2O Density H2O Volume = H2O 1.587 1010 mL Volume = H2O 4.194 106 gal From the balanced chemical reaction, 6 moles of O2 are produced from 6 moles of carbon dioxide: Mole O2 Mole . CO2 6 6 Mole = O2 1.057 109 mole MW O2 . . ( ) 2.15.9994 gm mole 1 Mass O2 Mole . O2 MW O2 Mass = O2 3.384 1010 gm Notice that this is identical to the mass of O2 used in the combustion reaction. All the oxygen is recovered by the tree. S.E. Van Bramer Widener University 11/4/97 From the balanced chemical reaction, 1 mole of cellulose is produced from 6 moles of carbon dioxide: Mole cellulose Mole . CO2 1 6 Mole = cellulose 1.762 108 mole MW cellulose . . ( ) 12.011.6 1.00794.10 15.9994.5 gm mole 1 Mass cellulose Mole . cellulose MW cellulose Mass = cellulose 2.858 1010 gm Assuming that a tree weighs 2 tons and is all cellulose: tree 2. ton tree = 1.814 106 gm Mass = cellulose 2.857 107 kg 1. tree 1.814.10 . 6 gm Mass = cellulose 15749 tree So from this "back of the envelope" calculation, about 16 thousand trees must be grown to absorb the carbon dioxide produced in one day by this power plant. 3.A typical automobile gets 30 miles per gallon of gas and drives 12,000 miles every year. Assuming that octane (C8H18, density 0.7025 g cm-1) is a principal component of gasoline; a.How much oxygen is required for a car to run for 1 year? b.How much CO2 is produced by the car in 1 year? c.How many trees are required to remove the CO2 produced by the car in 1 year? Let's start with a balanced reaction: 2 C8H18 + 25 O2 --> 16 CO2 + 18 H2O Next calculate the amout of octane used: mileage 30.mi.gal 1 distance 12000.mi volume gas distance mileage volume = gas 4 102 gal volume = gas 1.514 106 mL S.E. Van Bramer Widener University 11/4/97 density gas 0.7025.gm.cm 3 Mass gas density . gas volume gas Mass = gas 1.064 106 gm MW octane . . ( ) 12.011.8 1.00794.18 gm mole 1 Mole octane Mass gas MW octane Mole = octane 9.312 103 From the balanced chemical reaction, 25 moles of O2 are required for 2 moles of octane: Mole O2 Mole . octane 25 2 Mole = O2 1.164 105 mole MW O2 . . ( ) 2.15.9994 gm mole 1 Mass O2 Mole . O2 MW O2 Mass = O2 3.725 106 gm Mass = O2 4.106 ton From the balanced chemical reaction, 16 moles of CO2 are produced by 2 moles of octane: Mole CO2 Mole . octane 16 2 Mass CO2 Mole . CO2 MW CO2 Mass = CO2 3.278 106 gm Mass = CO2 3.614 ton From the balanced chemical reaction, 1 mole of cellulose is produced from 6 moles of carbon dioxide: Mole cellulose Mole . CO2 1 6 Mole = cellulose 1.242 104 mole Mass cellulose Mole . cellulose MW cellulose Mass = cellulose 2.013 106 gm Mass = cellulose 1.1 tree S.E. Van Bramer Widener University 11/4/97 4.Modern instrumental techniques are capable of detecting lead in a milliliter sample at picomolar concentration. a.How many moles of lead are in the sample? b.What is the mass of lead in this sample? c.How many grams of sodium chloride would be required to precipitate all the lead in this sample as lead (II) chloride? d.What would the mass of the lead (II) chloride precipitate be? Calculate the amount of lead in the sample from the concentration and the total volume Concentration Pb 10 . . 12 mole liter 1 Volume Pb 1.mL Volume = Pb 1 10 3 liter Mole Pb Concentration . Pb Volume Pb Mole = Pb 1 10 15 mole MW Pb 207.2.gm.mole 1 Mass Pb MW . Pb Mole Pb Mass = Pb 2.072 10 13 gm First write out the balanced equation: Pb2+ + 2 NaCl --> PbCl2 + 2 Na1+ (Note: the lead is an ion in aqueous solution) From the balanced reaction, 2 moles of NaCl are required for each mole of Pb2+ Mole NaCl Mole . Pb 2 1 Mole = NaCl 2 10 15 mole MW NaCl . . (22.989768 35.4527) gm mole 1 MW = NaCl 58.442 gm.mole 1 Mass NaCl MW . NaCl Mole NaCl Mass = NaCl 1.169 10 13 gm From the balanced reaction, 1 mole of PbCl2 is produced for each mole of Pb2+ Mole PbCl2 Mole . Pb 1 1 Mole = PbCl2 1 10 15 mole MW PbCl2 . . (107.2) 2.35.4527 gm mole 1 MW = PbCl2 1.781 102 gm.mole 1 Mass NaCl MW . NaCl Mole NaCl Mass = NaCl 1.169 10 13 gm

Q1

When the following solutions are mixed, does a precipitate form? Write out the total, total ionic, and net ionic equations.

1. a. silver nitrate and rubidium chloride
2. b. lead nitrate and potassium chloride
3. c. mercury (I) nitrate and hydrochloric acid
4. d. calcium chloride and sodium carbonate
5. e. magnesium nitrate and calcium chloride
6. f. potassium sulfate and barium chloride

Q2

Precipitation Reactions and Solubility.

1. a. Step 1: 0.8765 g of silver (I) nitrate is placed in a 250 mL volumetric flask diluted to the mark with deionized water. Determine the concentration of each ion in solution.
2. b. Step 2: 1.8793 g of potassium chloride is placed in a 250 mL volumetric flask diluted to the mark with deionized water. Determine the concentration of each ion in solution.
3. c. Step 3: 50.0 mL of the silver (I) nitrate solution and 50.0 mL of the potassium chloride solution are mixed together in an erlenmyer flask. Determine the mass of any precipitate formed and the concentration of each ion in solution.

CHAPTER OVERVIEW

6: Reaction Kinetics

6.1: Chemical Kinetics

Skills to Develop

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

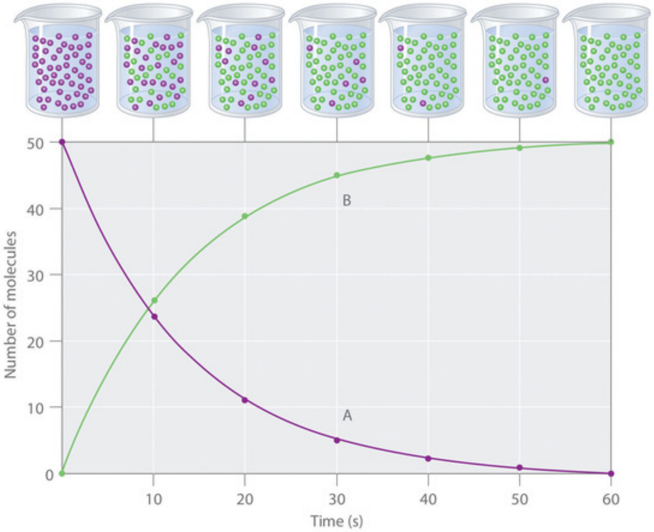


Figure $6.1.1$: *The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).*

The progress of a simple reaction (A → B) is shown in Figure $6.1.1$; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure $6.1.1$. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{6.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation $6.1.1$ is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation $6.1.1$ to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure $6.1.2$.

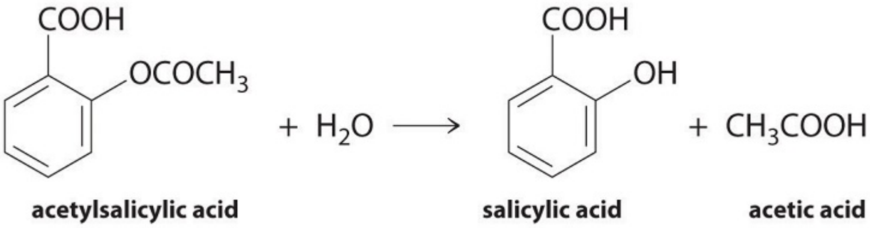


Figure $6.1.2$: *Hydrolysis of Aspirin reaction.*

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table $6.1.1$ and are shown in the graph in Figure $6.1.3$.

Table $6.1.1$: *Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C**

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table $6.1.1$ were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

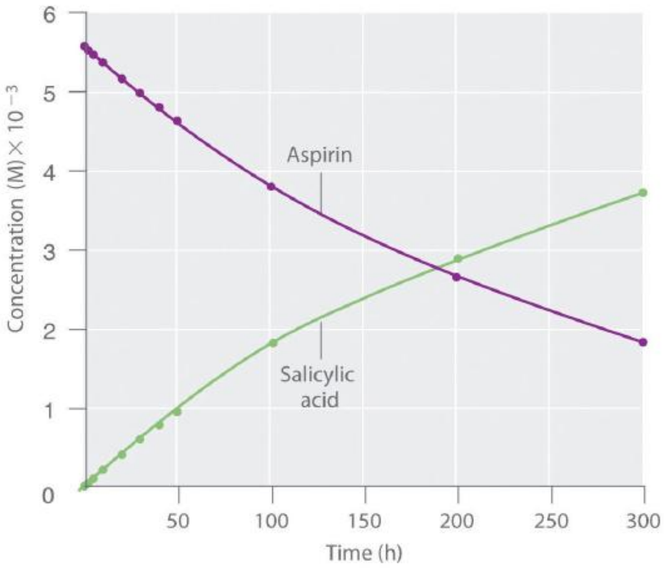


Figure $6.1.3$: *The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.*

6.2 The Effect of Concentration on Reaction Rate

Skills to Develop

- To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{2}$$

The proportionality constant (*k*) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of *k*, however, does not change as the reaction progresses under a given set of conditions.

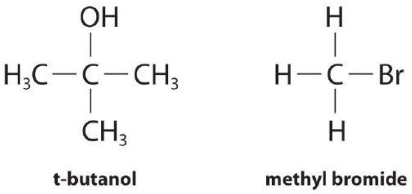
> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers *m* and *n*, respectively. The values of *m* and *n* are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers, but often are. For example, Equation 2 tells us that Equation 1 is *m*th order in reactant A and *n*th order in reactant B. It is important to remember that *n* and *m* are not related to the stoichiometric coefficients *a* and *b* in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: *m* + *n*.

It is important to realize that in kinetics, the term "order" is used in the mathematical sense, referring to the value of the exponent. For example, the equation $x^3 + y + z^2 = 0$, is said to be third order in x, first order in y, and second order in z. Thus "order", in kinetics, does **not** refer to which substance reacts "first" or "second".

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{3}$$

Combining the rate expression in Equation 2 with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{4}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{5}$$

Inserting the identities of the reactants into Equation 5 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{6}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 5 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{7}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value $5.15 \times 10^{-4}\ s^{-1}$ at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{8}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 8 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-] \tag{9}$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

Example 1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g) \tag{10}$$

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:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n \tag{11}$$

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:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2 \tag{12}$$

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise $1A$

The rate law for the reaction:

$$\text{H}_2(g) + 2\,\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \tag{13}$$

has been experimentally 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 $1B$

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:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OCOCH}_3 \longrightarrow \text{CH}_3\text{OCOCH}_3 + \text{CH}_3\text{CH}_2\text{OH} \tag{14}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\text{CH}_3\text{OH}] \tag{15}$$

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

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{16}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow products$ are given in Table 1.

Table* 1: Rate Data for a Hypothetical Reaction of the Form* $A + B \rightarrow products$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

The general rate law for the reaction is given in Equation 16. We can obtain *m* or *n* directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_3]^m[\text{B}_3]^n} \tag{17}$$

Inserting the appropriate values from Table 3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n} \tag{18}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m = 1.00$ M. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that *m* = 2 and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for *m*.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for *n*.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table 3,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n} \tag{19}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table 3 into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table 1 gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 3

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give

NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2NO + O_2 \longrightarrow 2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Determine the rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.
B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution:

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1} \tag{20}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1} \tag{21}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m+n)=3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Exercise 3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer:

rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ M^{-1}{\cdot}s^{-1}$

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. The rate constant (*k*) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

6.3: Reaction Mechanisms

Skills to Develop

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2C_8H_{18\,(l)} + 25O_2(g) \rightarrow 16CO_{2\,(g)} + 18H_2O_{(g)} \tag{6.3.1}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the mechanism of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> *The overall sequence of elementary reactions is the mechanism of the reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_2(g) + CO(g) \rightarrow NO_{(g)} + CO_{2\,(g)} \tag{6.3.2}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[NO_2]^2 \tag{6.3.3}$$

The fact that the reaction is second order in $[NO_2]$ and independent of $[CO]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[NO_2][CO]. \tag{6.3.4}$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

step 1	$\mathrm{NO_2 + NO_2 \xrightarrow{slow} NO_3 + NO}$	elementary reaction
step 2	$\underline{\mathrm{NO_3 + CO \rightarrow NO_2 + CO_2}}$	elementary reaction
sum	$\mathrm{NO_2 + CO \rightarrow NO + CO_2}$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

> *The sum of the elementary reactions in a reaction mechanism* ***must*** *give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as unimolecular; if there are two reactant molecules, it is bimolecular; and if there are three reactant molecules (a relatively rare situation), it is termolecular. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

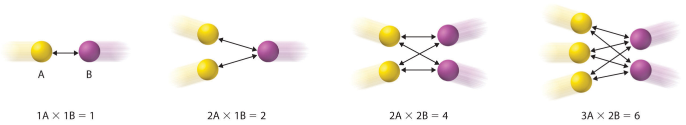


Figure 6.3.1: *The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step.*

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 6.3.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is rate = k[A]. For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 6.3.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is rate = k[A][B].

Table 6.3.1: *Common Types of Elementary Reactions and Their Rate Laws*

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = $k[A]^2$	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = $k[A]^2[B]$	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law* ***cannot*** *be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.

Rate-determining step. *The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow.*

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	rate $= k_1[NO_2]^2$ (predicted)
step 2	$\underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$	rate $= k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	rate $= k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 6.3.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO, N_2O_4 appears as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.
B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution:

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

Exercise 6.3.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2ICl(l) + H_2(g) \rightarrow 2HCl(g) + I_2(s)$$

The experimentally determined rate law is rate = $k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

step 1	$\mathrm{ICl + H_2 \xrightarrow{k_1} HCl + HI}$	$\text{rate} = k_1[\mathrm{ICl}][\mathrm{H_2}]$ (slow)
step 2	$\underline{\mathrm{HI + ICl \xrightarrow{k_2} HCl + I_2}}$	$\text{rate} = k_2[\mathrm{HI}][\mathrm{ICl}]$ (fast)
sum	$\mathrm{2ICl + H_2 \rightarrow 2HCl + I_2}$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

Example 6.3.2 : NO with H_2

Assume the reaction between NO and H_2 occurs via a three-step process:

step 1	$\mathrm{NO + NO \xrightarrow{k_1} N_2O_2}$
step 2	$\mathrm{N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O}$
step 3	$\mathrm{N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O}$

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: rate = $k[NO]^2[H^2]$?

Answer:

- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$
- Step 3: $rate = k_3[N_2O][H_2]$

The overall reaction is then

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g) \tag{6.3.5}$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[N_2O_2] = k_1[NO]^2$. Substituting $k_1[NO]^2$ for $[N_2O_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

6.4: The Effect of Temperature on Reaction Rate

Skills to Develop

The Learning Objective of this Module is to understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. According to the collision model, a chemical reaction can occur only when the reactant molecules, atoms, or ions collide with more than a certain amount of kinetic energy and in the proper orientation. The collision model explains why, for example, most collisions between molecules do not result in a chemical reaction. Nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO_2 a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide. The collision model also explains why such chemical reactions occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates.

Activation Energy

Previously, we discussed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. The simple observation that the molecules travel faster as they get warmer does not explain why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy (E_a)**. We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \tag{6.4.1}$$

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

The reaction rate, not the rate constant, will vary with concentration. The rate constant, however, does vary with temperature. Figure ***Table* 6.4.1** shows a plot of the rate constant of the reaction of NO with O_3 at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature. In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

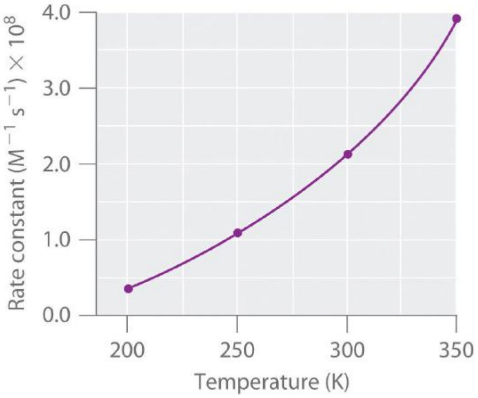


***Figure 6.4.1**: Rate Constant versus Temperature for the Reaction of NO with O_3 The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases.*

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the activation energy, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> *Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.*

Graphing Energy Changes during a Reaction

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 6.4.2 shows a plot for the NO–O_3 system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔH, if the reaction is carried out at constant pressure) is negative, which means that the reaction releases energy. (In this case, ΔH is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

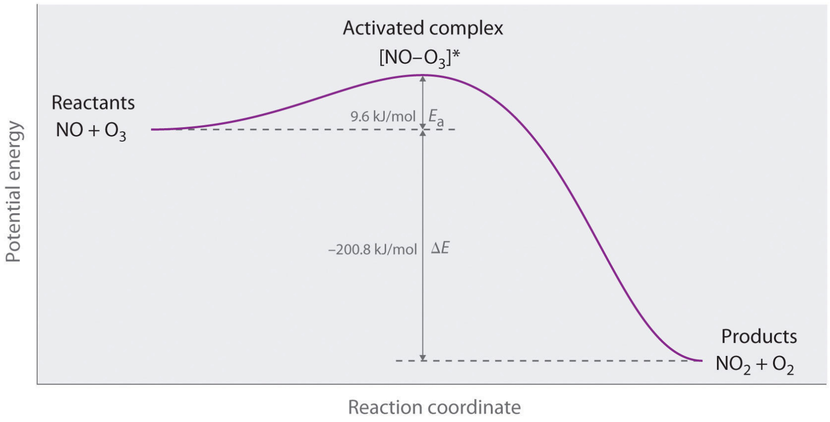


Figure **6.4.2***: Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex.*

Part (a) in Figure 6.4.3 illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, part (b) in Figure 6.4.3 illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta H > 0$. Although the energy changes that result from a reaction can be positive, negative, or even zero, in all cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is always positive.

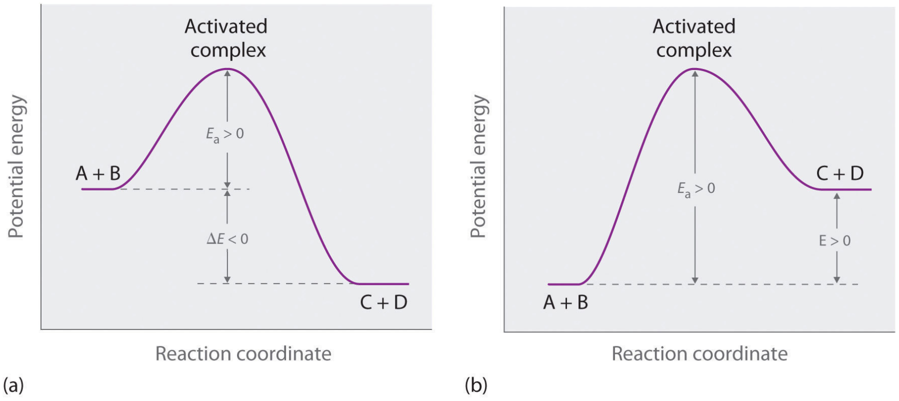


Figure **6.4.3***: Differentiating between E_a and ΔH. The potential energy diagrams for a reaction with (a) $\Delta H < 0$ and (b) $\Delta H > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. E_a is always positive. For a reaction such as the one shown in (b), E_a must be greater than ΔH.*

> *For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.*

Whereas Δ*H* is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.

Even when the energy of collisions between two reactant species is greater than E_a, however, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 6.4.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a, most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the **steric factor (*p*)**, and, in general, its value can range from 0 (no orientations of molecules result in reaction) to 1 (all orientations result in reaction).

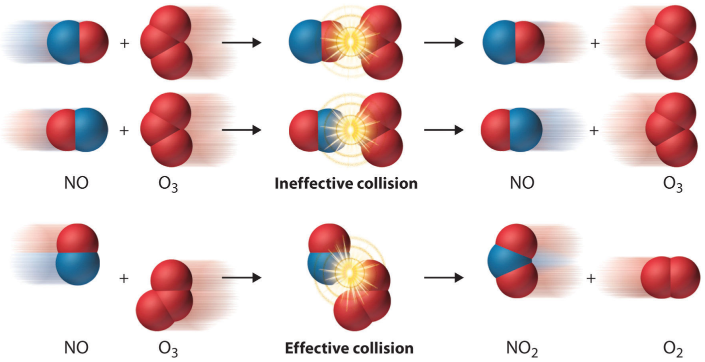


Figure **6.4.4***: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the* *terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$.*

The Arrhenius Equation

Figure 14.5.5 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

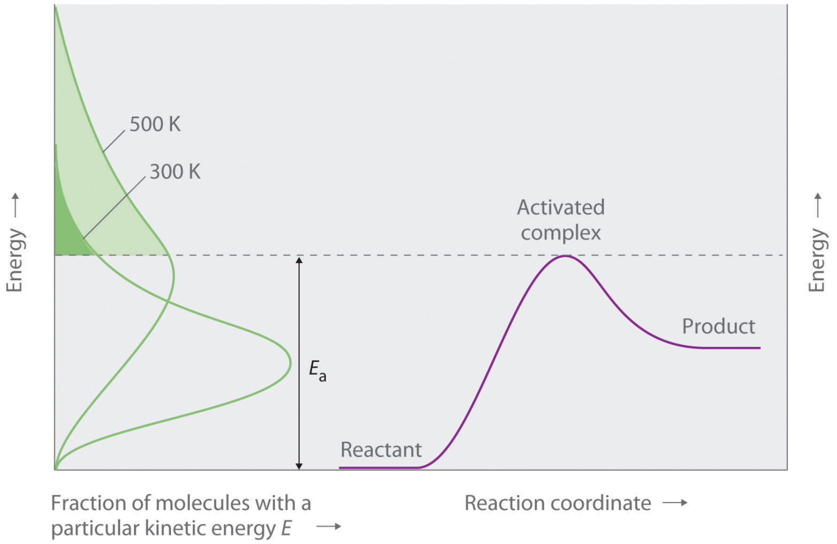


***Figure* 6.4.5**: *Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have E > E_a and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K.*

For an A + B elementary reaction, all the factors that affect the reaction rate can be summarized in a single series of relationships:

rate = (collision frequency)(steric factor)(fraction of collisions with $E > E_a$)

where

$$rate = k[A][B] \tag{6.4.2}$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, *A*, called the **frequency factor**:

$$k = Ae^{-Ea/RT} \tag{6.4.3}$$

The frequency factor is used to convert concentrations to collisions per second. Because the frequency of collisions depends on the temperature, *A* is actually not constant. Instead, *A* increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time. Equation 6.4.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where *T* is the absolute temperature (in K) and *R* is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 6.4.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) = \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{6.4.4}$$

Equation 6.4.4is the equation of a straight line, $y = mx + b$, where $y = \ln k$ and $x = 1/T$. This means that a plot of ln k versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of ln A. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters.

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. A minimum energy (activation energy,E_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$.

6.5 Catalysts

Skills to Develop

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure 1). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

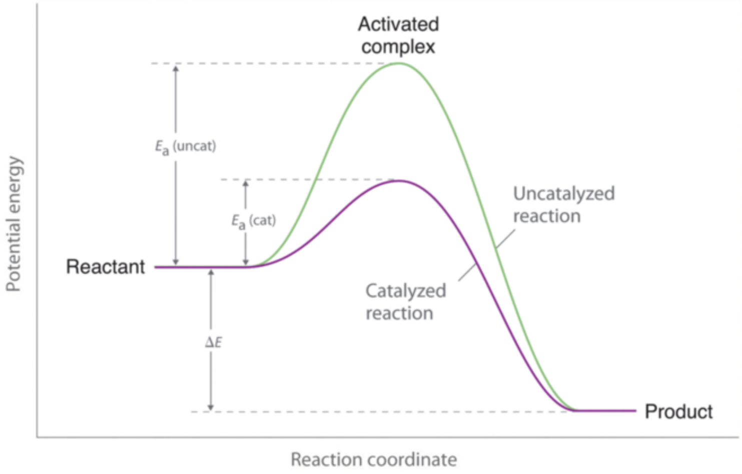


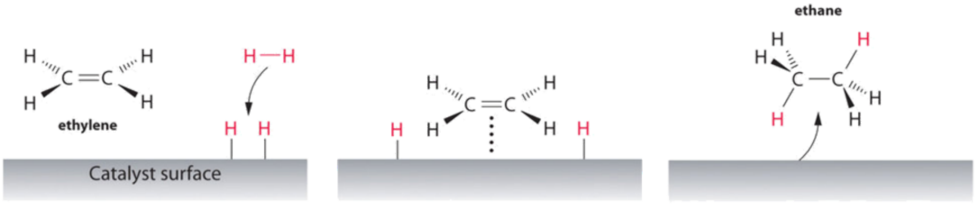
***Figure 1**: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔH).*

> *A catalyst affects E_a, not ΔH.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst’s efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

***Figure 2**: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released.*

Figure 2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

***Table 1**: Some Commercially Important Reactions that Employ Heterogeneous Catalysts*

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3

water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H$	CH ac

catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 2: *Some Commercially Important Reactions that Employ Homogeneous Catalysts*

Commercial Process	**Catalyst**	**Reactants**	**Final Product**
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R–O–O–H$	
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO

adiponitrile process	Ni/PR_3complexes	2HCN + CH_2=CHCH=CH_2	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon

olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$–(CH_2CH_2–)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 3).

Figure 3: *A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of* \(\ce{H2O2}\).

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

CHAPTER OVERVIEW

7: Equilibrium and Thermodynamics

7.1: The Concept of Dynamic Equilibrium

Skills to Develop

- To understand what is meant by chemical equilibrium.

Two Methods to Describe the Likely Result of a Chemical Reaction

In the previous chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. We will learn two "languages" to describe the extent of a reaction. First we will describe the final, likely state of a chemical reaction in terms of the ratio of the amount of products to the amount of reactants at equilibrium. Then we will apply the principles of **thermodynamics** to show how energy flow determines the likely amount of product made by a reaction when it reaches dynamic equilibrium.

Equilibrium

For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.

Figure 7.1.1: *Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. Figure used with permission from Wikipedia (CC BY-SA 3.0; Eframgoldberg).*

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 7.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{7.1.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \xrightarrow{k_f} 2\,NO_2(g) \tag{7.1.2}$$

and reverse reaction

$$2\,NO_2(g) \xrightarrow{k_r} N_2O_4(g) \tag{7.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium, as section 7. 4 demonstrates.

Figure $7.1.2$ shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure $7.1.2a$), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure $7.1.2b$). Thus equilibrium can be approached from either direction in a chemical reaction.

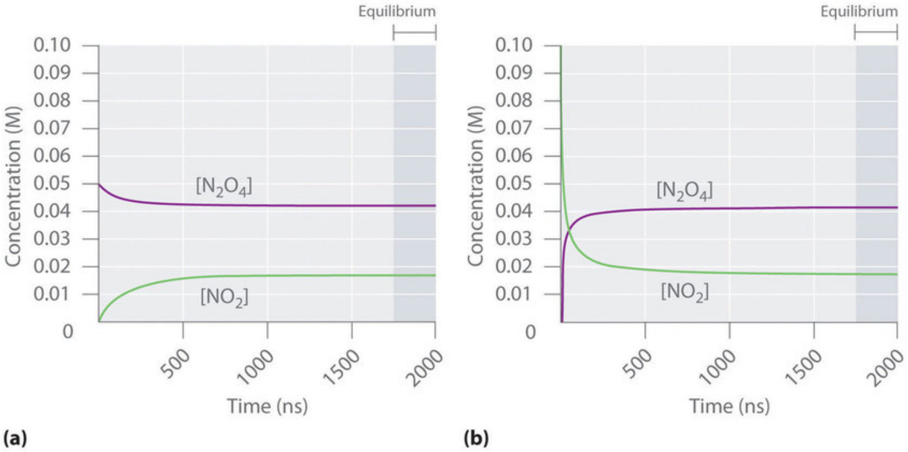


Figure $7.1.2$: *The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium.*

Figure $7.1.3$ shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases. Eventually, the forward and reverse reaction rates become identical, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

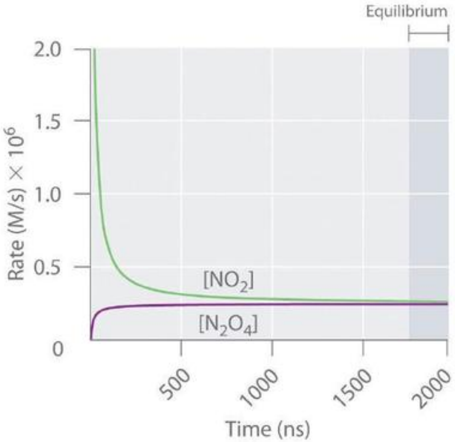


***Figure 7.1.3**: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 7.1.2*

Initially, the rate of dimerization of $\mathrm{NO_2}$ (reverse reaction) is quite rapid, but this rate decreases over time as the concentration of $\mathrm{NO_2}$ decreases. Because the initial concentration of $\mathrm{N_2O_4}$ is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the $\mathrm{N_2O_4}$ concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ no longer change.

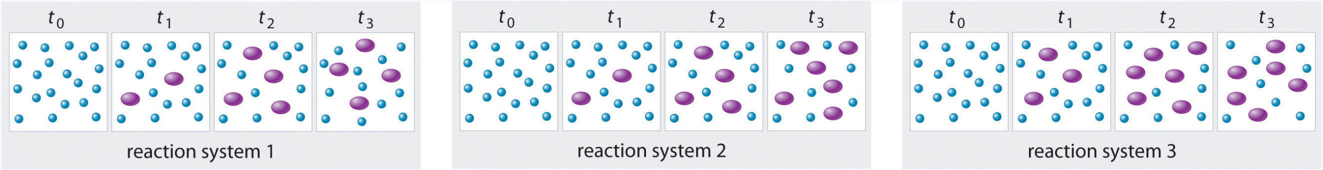
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 7.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B \tag{7.1.4}$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

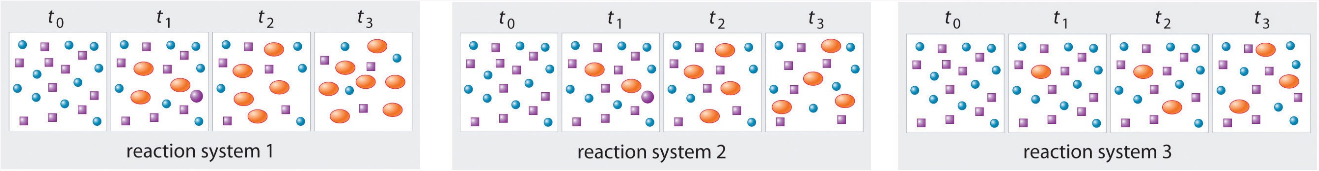
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 7.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer

system 2

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

7.2 The Equilibrium Constant

Skills to Develop

- To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{2}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{4}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

Many reactions occur by a multi-step mechanism, and so the equilibrium composition can not be so easily derived as shown in the above example. However it is universally true that the numerical value of the equilibrium constant of a system at equilibrium at a specific temperature will always have a constant value, as shown below.

Table 1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 3. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

***Table 1**: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C*

	Initial Concentrations		**Concentrations at Equilibrium**		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{6}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{7}$$

where K is the equilibrium constant for the reaction. Equation 6 is called the equilibrium equation, and the right side of Equation 7 is called the equilibrium constant expression. The relationship shown in Equation 7 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 1 indicate a reaction that is product-favored at equilibrium (-ΔG^o). If K is greater than 10^3, the reaction has a strong tendency for the reactants to form products. In this case, chemists say that equilibrium lies far to the right as written, favoring the formation of a great deal of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 1 indicate a reaction that is reactant-favored at equilibrium (+ΔG^o). If K is less than 10^{-3} the reaction has a very slight tendency for the reactants to form products, so that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 2: *Equilibrium Constants for Selected Reactions**

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	$4.6\times^{10-7}$
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 2 that equilibrium constants have no units, even though Equation 7 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 8, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{mol}{\cancel{L}}}{\frac{mol}{\cancel{L}}} \tag{8}$$

> *In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.*

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{10}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 3 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants $\rightleftharpoons$ products.

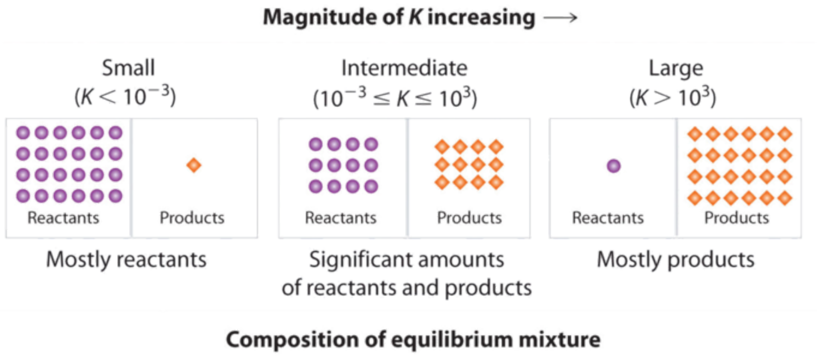


Figure 3: *The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.*

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

Example 1: equilibrium constant expressionS

Write the equilibrium constant expression for each reaction.

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{11}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{12}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{13}$$

Exercise 1

Write the equilibrium constant expression for each reaction.

a. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
b. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
c. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{14}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{15}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a [B]^b}{[C]^c [D]^d} \tag{16}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{17}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{18}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> *The equilibrium constant for a reaction written in reverse is the inverse of the equilibrium constant for the reaction as written originally.*

Example 3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{19}$$

What is the equilibrium constant for $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$ at 745 K?

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for the reverse reaction

Strategy:

Write the equilibrium constant expression for the given reaction and for the reverse reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118 \tag{20}$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47 \tag{21}$$

Exercise 3

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

is 7.90×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

Answer

1.27×10^{-5}

Heterogeneous Equilibria

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid, or the reaction of a solute with the solvent to form a new, different solute. In these heterogeneous equilibria, the pure liquids and pure solids are assigned an activity of 1.

This standard convention causes quite a bit of confusion because the treatment of the activity of a pure solid, pure liquid, or solvent differs from the treatment of the activity of a gas or a solute in a mixture. The true law of mass action is a ratio of activities of all the reactants and products. However, to simplify measurements and calculations, the activity of any gas or any solute can be approximated by its molarity. The activity of a pure solid or a pure liquid or a solvent is never approximated by its concentration. Instead, the activity of the pure solid, or pure liquid, or solvent is defined as having a value of 1.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{22}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2} a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{23}$$

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described above will reach chemical equilibrium only if excess solid carbon has been added so that some solid carbon is still present once the system has reached equilibrium. As shown in Figure 4, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

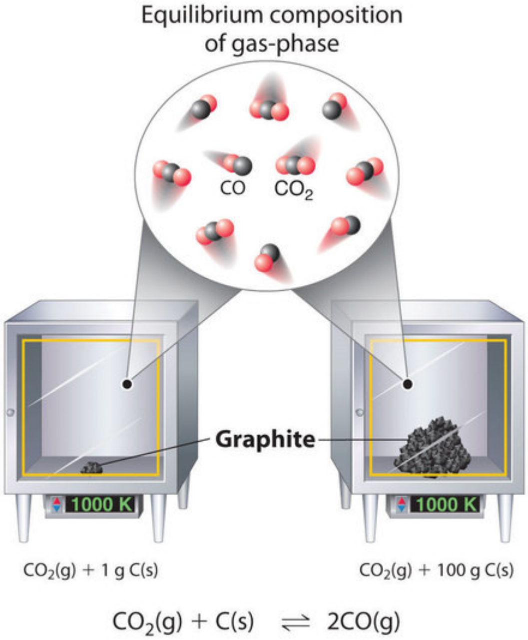


***Figure 4**: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.*

Example 4

Write each expression for K for the following equilibrium reactions.

$$PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)} \tag{24}$$

$$Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)} \tag{25}$$

Given: balanced equilibrium equations

Asked for: expression for K

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the activities of the products and reactants, each raised to its coefficient in the chemical equation. Then substitute the appropriate concentration or activity to arrive at the common form of the law of mass action

Solution:

The first reaction contains a pure solid PCl_5 and a pure liquid PCl_3. As pure substances, their activities are defined as "1", so they do not appear explicitly in the equilibrium constant expression. So

$$K=\frac{a_{PCl_5}}{a_{PCl_3}a_{Cl_2}}=\frac{1}{(1)[Cl_2]}=\frac{1}{[Cl_2]} \tag{26}$$

The second reaction contains two pure solids Fe_3O_4 and Fe, which both have an activity defined as "1", and so do not appear explicitly in the equilibrium constant expressions. The concentrations of the two gases do, however, appear in the expressions:

$$K=\frac{a^3_{Fe}a^4_{H_2O}}{a_{Fe_3O_4}a^4_{H_2}}=\frac{(1)^3[H_2O]^4}{(1)[H_2]^4}=\frac{[H_2O]^4}{[H_2]^4} \tag{27}$$

Exercise 4

EXERCISE 7

Write the expression for K for the following reactions.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)}+CO_{2(g)} \tag{28}$$

$$C_6H_{12}O_{6(s)}+6O_{2(g)} \rightleftharpoons 6CO_{2(g)}+6H_2O_{(g)} \tag{29}$$

Answer

$$K=\frac{a_{CaO}a_{CO_2}}{a_{CaCO_3}}=\frac{(1)[CO_2]}{1}=[CO_2] \tag{30}$$

$$K=\frac{a^6_{CO_2}a^6_{H_2O}}{a_{C_6H_{12}O_6}a^6_{O_2}}=\frac{[CO_2]^6[H_2O]^6}{(1)[O_2]^6}=\frac{[CO_2]^6[H_2O]^6}{[O_2]^6} \tag{31}$$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms.*

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{32}$$

Contributors

Modified by Tom Neils (Grand Rapids Community College)

7.3: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations

Skills to Develop

- To solve quantitative problems involving chemical equilibriums.

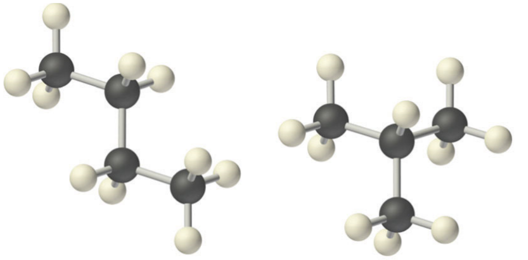
There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw earlier that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



n-butane isobutane (2-methylpropane)

This reaction can be written as follows:

$$\text{n−butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.3.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = \frac{0.041\ M}{0.016\ M} = 2.6 \tag{7.3.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 7.3.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

SOLUTION

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

Exercise 7.3.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K for this reaction.

Answer

$K = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example $7.3.2$ shows one way to do this.

Example 7.3.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

SOLUTION

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K=\frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$ The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$ We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \ mol\ \cancel{Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \ mol\ \cancel{Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \ mol\ \cancel{Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \ mol\ \cancel{Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444 M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise 7.3.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature?

Answer

$K = 0.105$

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 7.3.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example $7.3.2$.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.3.3}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{7.3.4}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{7.3.5}$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x \tag{7.3.6}$$

$$x + 2.6x = 2.6 \tag{7.3.7}$$

$$x = 0.72 \tag{7.3.8}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{7.3.9}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{7.3.10}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{7.3.11}$$

This is the same K we were given, so we can be confident of our results.

Example $7.3.3$ illustrates a common type of equilibrium problem that you are likely to encounter.

Example 7.3.3: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

SOLUTION

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.0150 - x)$	$(0.0150 - x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x)} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150 - x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise 7.3.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f = 0.270\ M$
- $[H_2]_f = [I_2]_f = 0.037\ M$

In Example $7.3.3$, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example $7.3.4$.

Example 7.3.4

In the water–gas shift reaction shown in Example $7.3.3$, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

SOLUTION

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example $7.3.3$, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x=\frac{-b\pm\sqrt{b^2-4ac}}{2a}=\frac{-0.127\pm\sqrt{(0.127)^2-4(0.894)(-0.0382)}}{2(0.894)}$$

$$x=0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O]=\Delta[CO]=+0.148M$, and $\Delta[H_2]=\Delta[CO_2]=-0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[=[H_2]_i+\Delta[H_2]=0.570\ M-0.148\ M=0.422M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=0.632\ M-0.148\ M=0.484M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=0\ M+0.148\ M=0.148\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=0M+0.148\ M=0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.148)^2}{(0.422)(0.484)}=0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise 7.3.4

The exercise in Example 7.3.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K=54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

- $[H_I]_f=0.0882\ M$
- $[H_2]_f=0.156\ M$
- $[I_2]_f=9.2\times10^{-4}M$

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

Contributors

Modified by Tom Neils (Grand Rapids Community College)

7.4 Predicting the Direction of a Reaction

Skills to Develop

- To predict in which direction a reaction will proceed.

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a Quantity called the reaction Quotient (Q). The expression for the reaction Quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{2}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{3}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

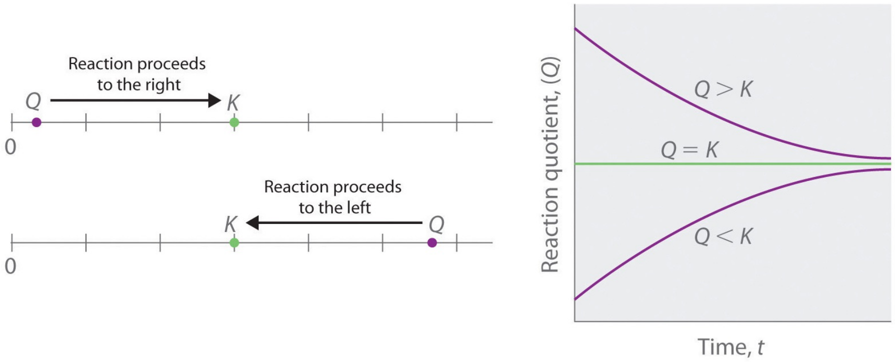
$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{4}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Experiment	$[\boldsymbol{NO_2}]\ (\boldsymbol{M})$	$[\boldsymbol{N_2O_4}]\ (\boldsymbol{M})$	$\boldsymbol{Q = \frac{[NO^2]^2}{[N^2O^4]}}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, K can be greater than, less than, or equal to Q.

Comparing the magnitudes of K and Q enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K. If $K = Q$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $K > Q$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $K < Q$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 1.



(a) Q versus *K*, t_0 to *t*

(b) Q versus *K*, t_0 to t_∞

***Figure* 1**: *Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of* $K < Q$, $K > Q$, *and* $K = Q$.

> *If* $K > Q$, *the reaction will proceed to the right as written. If* $K < Q$, *the reaction will proceed to the left as written.*
>
> *If* $K = Q$, *then the system is at equilibrium.*

Example 1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \tag{5}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0 × 10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 2 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M \tag{6}$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B We now compute Q and compare it with K:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6} \tag{7}$$

Because $K = 2.4 \times 10^{-4}$, we see that $K > Q$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

Exercise 2

In the water–gas shift reaction introduced in Example 1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \tag{8}$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$. Since $K < Q$, the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $K = Q$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_{3(s)} \rightleftharpoons PbO_{(s)} + CO_{2(g)} \tag{9}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 3, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only CO2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (K < Q). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 9 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (K > Q). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 9 will therefore proceed to the right as written, until $[CO_2] = K$.

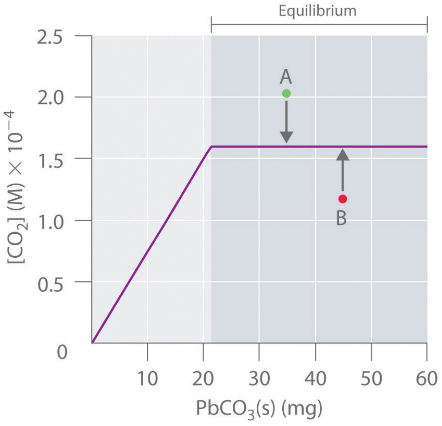


Figure 2: *The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.*

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)} \tag{10}$$

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 10 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (K > Q). Thus the reaction in Equation 10 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture (K < Q). Thus the reaction in Equation 10 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

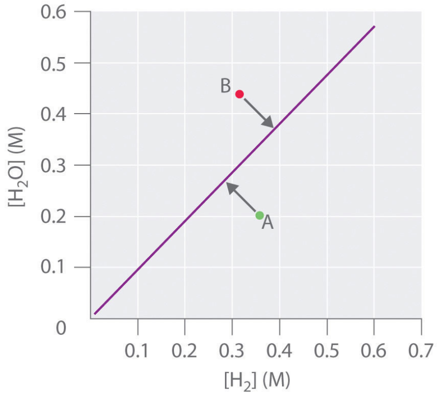


Figure 3*: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.*

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{11}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 4. As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 4) corresponds to $K > Q$, and the reaction in Equation 11 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 11) corresponds to $K < Q$, and the reaction in Equation 11 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

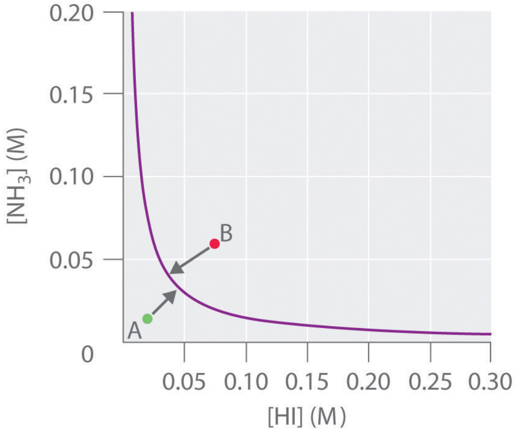


***Figure 4**: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.*

Summary

The reaction quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. The reaction Quotient (Q) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $K = Q$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Contributors

Modified by Tom Neils (Grand Rapids Community College)

7.5 Le Châtelier’s Principle: How a System at Equilibrium Responds to Disturbances

Skills to Develop

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier’s principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (a change in concentration of one of the species in the law of mass action) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if K > Q) or the reactants (if K < Q) until Q returns to the same value as K. This process is described by Le Chatelier's principle.

Le Chatelier's principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in the value of Q; the reaction will shift to re-establish K = Q

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> *A chemical system at equilibrium can be* ***temporarily*** *shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.*

The stress on the system in Figure 7.9.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause K to be larger than *Q*). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.

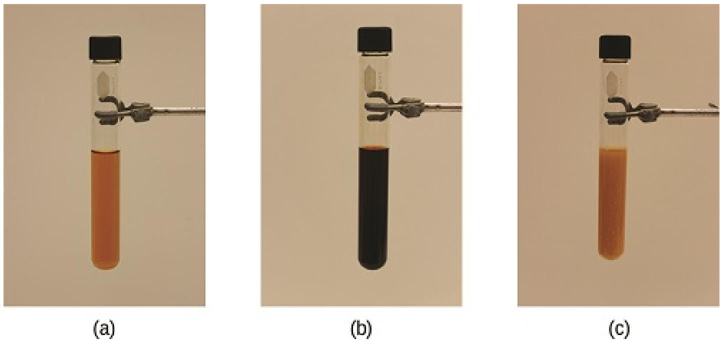


Figure 7.9.1: *(a) The test tube contains 0.1 M* Fe^{3+}*. (b) Thiocyanate ion has been added to solution in (a), forming the red* $Fe(SCN)^{2+}$ *ion:* $Fe^{2+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$ (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^- as the white solid AgSCN: $Ag^+_{(aq)} + SCN^-_{(aq)} \rightleftharpoons AgSCN_{(s)}$. *The decrease in the* SCN^- *concentration shifts the first equilibrium in the solution to the left, decreasing the concentration of the* $Fe(SCN)^{2+}$*, and lightening color. (credit: modification of work by Mark Ott).*

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_g$$

K = 50.0 at 400^{o}C

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221$ M and [HI] = 1.563 M is at equilibrium; for this mixture, K = Q. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442$ M), the reaction will shift so that equilibrium is reattained with new concentrations of $[H_2]$, $[I_2]$, and [HI]:

$[H_2] = 0.374$ M

$[I_2] = 0.153$ M

[HI] = 1.692 M

This gives

$$Q=\frac{[HI]^2}{[H_2][I_2]}$$

$$Q=\frac{[1.692]^2}{[0.374][0.153]}$$

$$Q=50.0=K$$

Even though we have stressed this system by introducing additional H_2, the stress is relieved as the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of unreacted I_2, and forming additional HI. There are new concentrations of all three substances, but the ratio of these concentrations, as described by the law of mass action, is once again equal to 50.0, because that is the fixed value of K for this reaction at this temperature.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. In addition, the change in pressure must cause a change in concentration of the substances involved in the reaction. The only practical way to cause a concentration change by making a pressure change is to change the size of the container holding the gases. Some changes to total pressure, such as adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens if we shrink the flask, thus increasing the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2NO_{(g)}+O_{2(g)}\rightleftharpoons NO_{2(g)}$$

Increasing the pressure causes the concentration of all of the gases to **increase** (because molarity is moles per Liter, and you just decreased the volume). To reattain equilibrium, the reaction will shift to the right, the side with fewer moles of gas. This shift to the right happens because it decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. Thus, the shift to the right reduces the total pressure exerted by the system and leads to new concentrations of all of the gases that, when plugged into the law of mass action, result in K = Q.

On the other hand, expanding the flask will cause a decrease in the pressure on the system, which means that the concentrations of all the gases **decrease**. To reattain equilibrium, the reaction will shift to the left, the side with more moles of gas. This shift to the left happens because it increases the total number of molecules in the system because each time two molecules of NO_2 are consumed, a total of three molecules of NO and O_2 are formed. Thus, the shift to the left increases the total pressure exerted by the system and and leads to new concentrations of all of the gases that, when plugged into the law of mass action, result in K = Q.

Now consider this reaction:

$$N_{2(g)}+O_{2(g)}\rightleftharpoons 2NO_{(g)}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not cause a shift away from equilibrium, because the value of Q will equal K throughout any pressure change.

Effect of Change in Temperature on Equilibrium

Changing concentration perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. In other words, Q will not equal K at the instant of the change. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \ \Delta H^o = -9.4\ kJ$$

Because this reaction is exothermic, we can write it with heat as a product:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} + heat$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of heat, one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in the reaction:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \ \Delta H^o = 57.2\ kJ$$

The positive ΔH value tells us that the reaction is endothermic and could be written:

$$heat + N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table 7.9.1

Table 7.9.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with fewer moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Example 7.5 $LeCh\hat{a}telier'sPrinciple.1$

Write an equilibrium constant expression for each reaction and use this expression to predict in which direction the reaction will shift to reattain equilibrium.

a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + O_{2(g)}$: the amount of HgO is doubled.
b. $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$: the concentration of H_2S is tripled
c. $n - butane_{(g)} \rightleftharpoons isobutane_{(g)}$: the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

a. Because HgO is a pure solid and Hg is a pure liquid, they both are assigned an activity of '1' and their amounts do not appear in the equilibrium constant expression. Thus, for this reaction, K = $[O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2 so no compensatory change is necessary. The reaction does not shift from equilibrium.

b. NH_4HS is assign a value of '1' in the equilibrium constant expression because it is a solid. Thus K = $[NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If the concentration of H_2S triples, for example, then the concentration of NH_3 must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations (Q) equals K. The reaction must shift left to reach equilibrium.

c. For this reaction K = $\frac{[isobutane]}{[n-butane]}$, so halving the concentration of isobutane means that the n-butane concentration must also decrease by about half if the system is to maintain equilibrium. The reaction must shift to the right to reach equilibrium.

Exercise 7.5 $LeCh\hat{a}telier'sPrinciple.1$

In which direction will the reaction shift if the stated stress is placed on the reaction at equilibrium?

a. $HBr_{(g)} + NaH_{(s)} \rightleftharpoons NaBr_{(s)} + H_{2(g)}$: the concentration of HBr is decreased by a factor of 3.
b. $6Li_{(s)} + N_{2(g)} \rightleftharpoons 2Li_3N_{(s)}$: the amount of Li is tripled.
c. $SO_{2(g)} + Cl_{2(g)} \rightleftharpoons SO_2Cl_{2(l)}$: the concentration of Cl_2 is doubled.

Answer

a. The reaction will shift left to reattain equilibrium because you removed reactant.

b. The reaction will not shift because Li is a solid

c. The reaction will shift to the right because you added a reactant.

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations. The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements as shown above. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

Figure 7.9.2: *The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.*

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable to a majority of plants due the tremendous stability of the nitrogen-nitrogen triple bond. Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Contributors

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

7.6: The First Law of Thermodynamics

Skills to Develop

- To calculate changes in internal energy

Thermodynamics

We will now apply the principles of **thermodynamics** to show how energy flow determines the likely amount of product made by a reaction when it reaches dynamic equilibrium. To do so, we will need to do a bit of a review of definitions.

System versus Surrounding

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure $7.6.1$). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

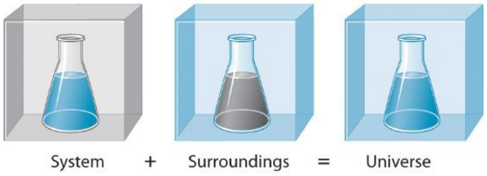


***Figure $7.6.1$:** A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.*

Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. A truly isolated system does not actually exist, however, because energy is always exchanged between a system and its surroundings, although this process may take place very slowly. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure $7.6.2$). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

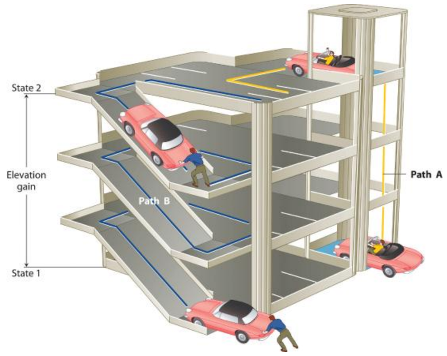


***Figure 7.6.2**: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are not state functions.*

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (Figure 7.6.3). The balanced chemical equation for the reaction is as follows:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) \tag{7.6.1}$$

***Figure 7.6.3**: The thermite reaction produces so much heat that the iron it produces comes out molten, a property that makes this reaction useful in welding. Image by Kingfisher [CC BY-SA 3.0 (https://creativecommons.org/licenses/by-sa/3.0)], from Wikimedia Commons.*

We can also write this chemical equation as

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) + \text{heat} \tag{7.6.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (***q***) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$heat + H_2O_{(s)} \rightarrow H_2O_{(l)} \tag{7.6.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 7.6.2 and 7.6.3 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

The First Law

The relationship between the energy change of a system and that of its surroundings is given by the **first law of thermodynamics**, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{7.6.4}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{7.6.5}$$

where U represents energy, and the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/ O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{7.6.6}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because of the first law, we can determine ΔU for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings. Work, w, may come in different forms, but it too can be measured.

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**. The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done.

Contributors

Modified by Tom Neils (Grand Rapids Community College)

7.7: Enthalpy: The Heat Evolved in a Chemical Reaction at Constant Pressure

Skills to Develop

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just PV *work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu(s) + 4\,HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,H_2O(l) + 2\,NO_2(g)} \tag{7.7.1}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure $7.7.1$). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure),

$$w = -P\Delta V \tag{7.7.2}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

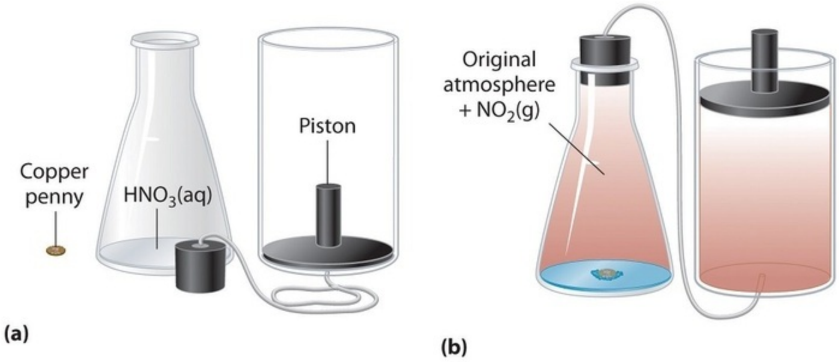


***Figure $7.7.1$**: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO$_2$ gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.* (CC BY-NC-SA; anonymous)

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called **enthalpy** (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

$$H = U + PV \tag{7.7.3}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. So we can define a change in enthalpy (ΔH) accordingly

$$\Delta H = H_{final} - H_{initial}$$

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{7.7.4}$$

$$= \Delta U + \Delta PV \tag{7.7.5}$$

$$= \Delta U + P\Delta V \tag{7.7.6}$$

Substituting $q + w$ for ΔU (First Law of Thermodynamics) and $-w$ for $P\Delta V$ (Equation 7.7.2) into Equation 7.7.6, we obtain

$$\Delta H = \Delta U + P\Delta V \tag{7.7.7}$$

$$= q_p + \cancel{w} - \cancel{w} \tag{7.7.8}$$

$$= q_p \tag{7.7.9}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 7.7.9 we see that at constant pressure the change in enthalpy, ΔH of the system, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} \tag{7.7.10}$$

$$= q_p \tag{7.7.11}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *The ΔH for a reaction is equal to the heat gained or lost at constant pressure, q_p.*

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*, and
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

Bond breaking **always** requires an input of energy and is therefore an endothermic process, whereas bond making **always** releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure 7.7.2*a*). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure 7.7.2*b*). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.*

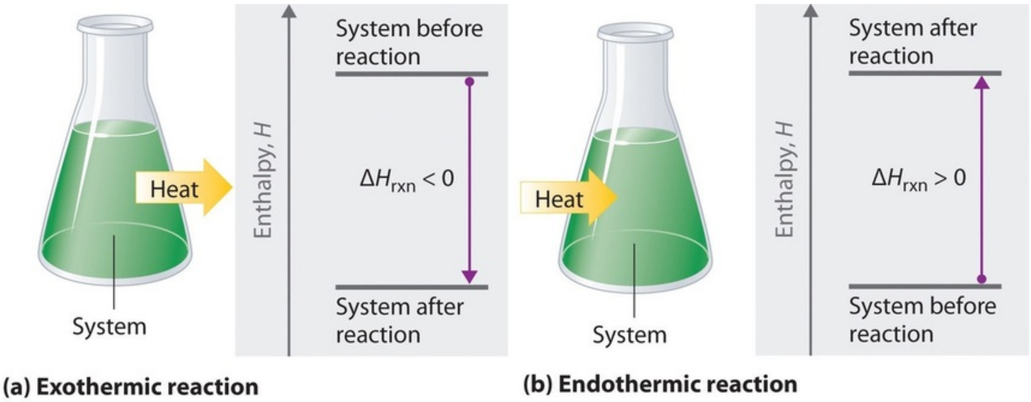


***Figure* $7.7.2$**: *The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.* (CC BY-NC-SA; anonymous)

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

  $$heat + H_2O(s) \rightarrow H_2O(l) \qquad \Delta H > 0$$
  $$H_2O(l) \rightarrow H_2O(s) + heat \qquad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.
- **Enthalpy is an extensive property (like mass).** The magnitude of Δ*H* for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 7.7.12, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

  $$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) + 815.5\ kJ \tag{7.7.12}$$

  Thus Δ*H* = −851.5 kJ/mol of Fe_2O_3. We can also describe Δ*H* for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 7.7.13, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

  $$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) \qquad \Delta H_{rxn} = -851.5\ kJ \tag{7.7.13}$$

  If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

  $$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{7.7.14}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example $7.7.1$.

Example 7.7.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$\mathrm{H_2O(s) \rightarrow H_2O(l)}$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.
B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given Δ*H* for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by Δ*H* (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \ \cancel{\text{metric ton}}\ \text{H}_2\text{O} \left(\frac{1000\ \ \cancel{kg}}{1\ \ \cancel{\text{metric ton}}}\right)\left(\frac{1000\ \ \cancel{g}}{1\ \ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \ g\ \cancel{H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol\,\text{H}_2\text{O}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{mol\ \cancel{H_2O}}\right)\left(5.55 \times 10^{10}\ \ mol\ \cancel{H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown below.

Possible sources of the approximately $3.34 \times 10^{11}\ kJ$ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

Alternatively, we can rely on ambient temperatures to slowly melt the iceberg. The main issue with this idea is the cost of dragging the iceberg to the desired place.

Exercise 7.7.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer

273 kJ

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, since enthalpy is a state function, all we have to know is the initial and final states of the reaction. This allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.

- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 7.7.1: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

Contributors

- Modified by Joshua Halpern (Howard University)
- Modified by Tom Neils (Grand Rapids Community College)

7.8 Quantifying Heat

Skills to Develop

- Distinguish the related properties of heat, thermal energy, and temperature

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." Temperature can also be thought of as a relative scale that allows us to determine the likely direction that heat will flow. 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 KE, and we say that the object is "cold" (Figure 1). 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.

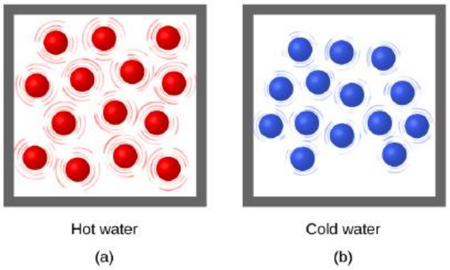


Figure 1: *(a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.*

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 is very likely to flow 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 (thermal equilibrium) (Figure 2).

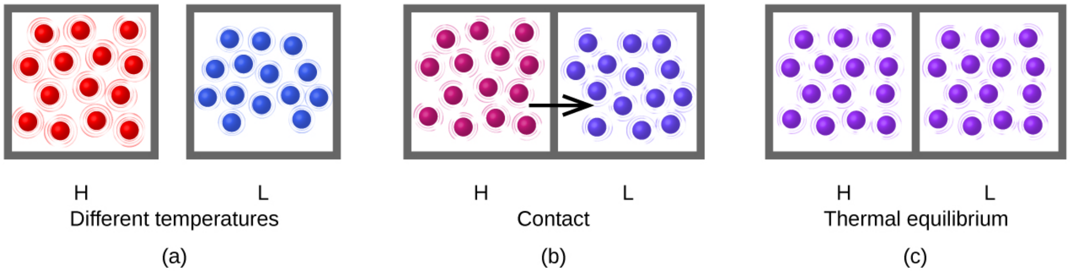


Figure 2: *(a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.*

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 3a). 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.

(a) (b)

***Figure 3**: (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 (also 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.

$$1\,cal \equiv 4.184\,J \tag{1}$$

Application: Heat can do more than increase temperature

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 4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

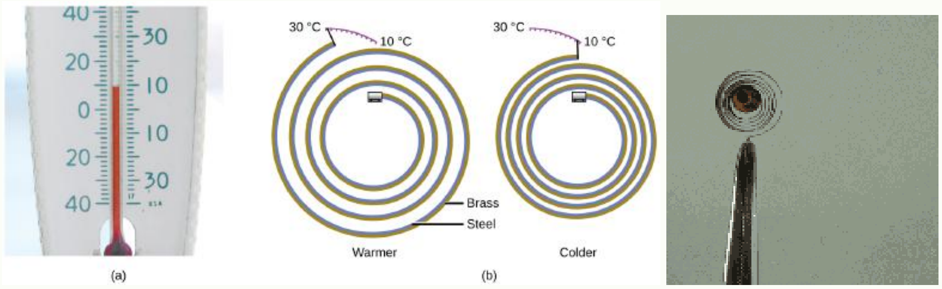


***Figure 4:** (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. 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). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)*

Direction of Heat Flow: Endothermic vs. Exothermic Processes

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{2}$$

We can also write this chemical equation as

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{3}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\mathrm{heat} + \mathrm{H_2O_{(s)}} \rightarrow \mathrm{H_2O_{(l)}} \tag{4}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

> *By convention, $q < 0$ for an exothermic reaction and $q > 0$ for an endothermic reaction.*

Exercise 1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. $\mathrm{NH_4Cl}$ is dissolved in water and the solution cools
d. the burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

Answer a

endothermic

Answer b

exothermic

Answer c

endothermic

Answer d

exothermic

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 3 and 4 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

Measuring Heat

Because Δ*H* is defined as the gain or loss of heat at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in processes at constant pressure) give Δ*H* values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure 5), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to Δ*H*, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{system} = -q_{calorimeter} = -mC\Delta T \tag{5}$$

The use of a constant-pressure calorimeter is illustrated in Example 1.

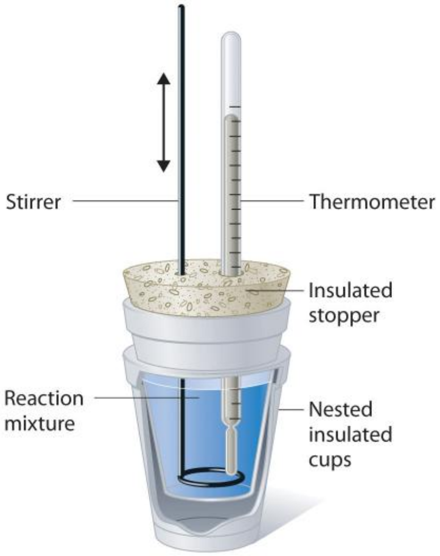


***Figure 5**: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.*

Example 1

If 2500. Joules of heat are transferred to a 25.5 gram solid with a specific heat capacity of $1.437 \frac{J}{g \cdot ^{o} C}$, by how many degrees Celsius will the temperature of the solid increase?

Given: mass of a solid, specific heat of solid, heat added.

Asked for: Temperature increase of solid, ΔT

Strategy:

Calculate change in temperature of water using Equation 7.3.1

Solution:

$$\Delta T = \frac{q}{mass \times C} = \frac{2500.J}{(25.5g)\left(1.437\frac{J}{g \cdot^o C}\right)} = 68.2^o C$$

Exercise 2

If 1507. Joules of heat are transferred to a 26.50 gram solid, and the temperature of the solid increases by 27.85°C, what is the specific heat capacity of the solid, in $\frac{J}{g \cdot^o C}$?

Answer

$$2.042\frac{J}{g \cdot^o C}$$

Example 2:

A 25.7 gram piece of solid is heated to 98.7 °C and then placed in 150.2 grams of water in a calorimeter at 20.2°C. After sitting for several minutes, the temperature of the water stabilizes at 22.3°C. The specific heat of water is 4.184 $\frac{J}{g \cdot^o C}$. Calculate the specific heat of the piece of solid.

Given: mass of a solid, mass of water, specific heat of water, initial and final temperatures.

Asked for: C of solid

Strategy:

A. Calculate change in heat of water using Equation 7.3.1

B. Calculate C of solid, given that $q_{water} = -q_{solid}$

Solution:

A. $q_{water} = 150.2g \times 4.184\frac{J}{g \cdot^o C} \times (22.3^o C - 20.2^o C) = 1320J$

B. $q_{solid} = -q_{water} = -1320J = 25.7g \times C_{solid} \times (22.3^o C - 98.7^o C)$

$$C_{solid} = \frac{-1320J}{(25.7g)(-76.4^o C)} = 0.672\frac{J}{g \cdot^o C}$$

Exercise 3

A 14.8 gram piece of solid is heated to 100.2 °C and then placed in 102 grams of water in a calorimeter at 21.3°C. After sitting for several minutes, the temperature of the water stabilizes at 22.9°C. The specific heat of water is 4.184 $\frac{J}{g \cdot^o C}$. Calculate the specific heat of the piece of solid.

Answer

$$0.597\ \frac{J}{g \cdot^o C}$$

Heating and Cooling Curves for Water

Freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 6 shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

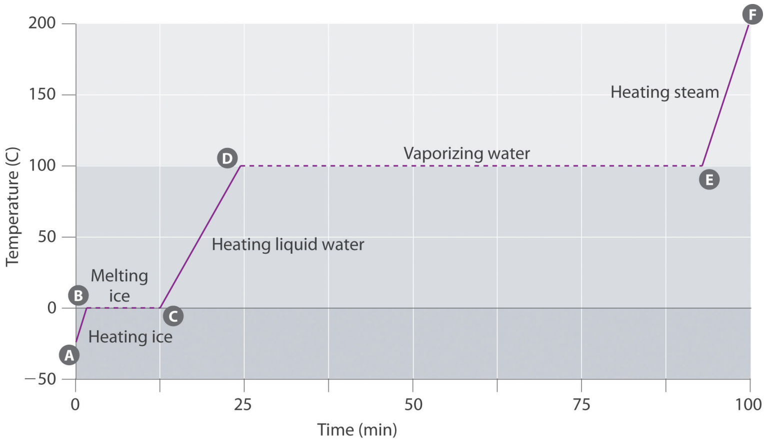


Figure 6: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure 6, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 6, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 7 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 6, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

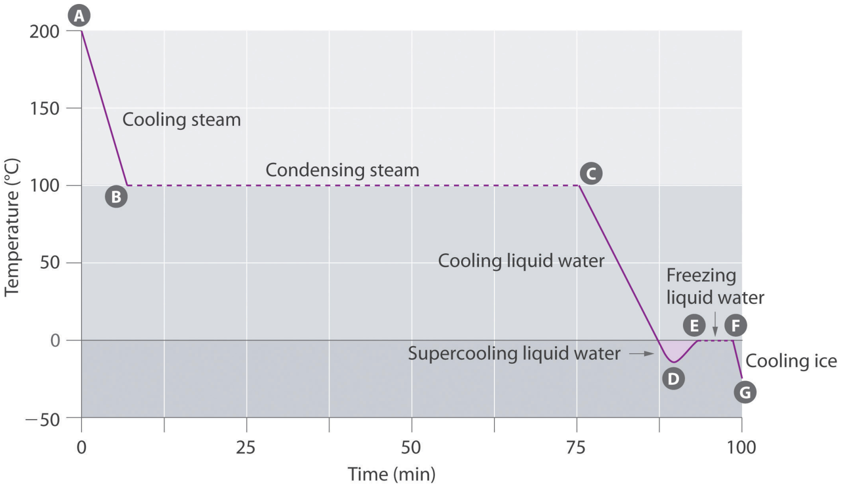


Figure 7*: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.*

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

Example 3: Cooling Hot Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost (Equation 5.39) to obtain the final temperature of the mixture.

Solution:

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T \tag{6}$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

Exercise 4: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it’s just frozen water. To understand the guide’s recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body’s internal temperature of 37°C. Use the data in Example 3

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Contributors

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

7.9: Entropy and the Second Law of Thermodynamics

Skills to Develop

- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (U). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. This information, however, does not tell us whether a particular process or reaction will occur spontaneously. (In chemistry, the word **spontaneous** means "very likely to proceed in the forward direction, as written, in order to reach equilibrium.")

Let’s consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process is very unlikely to occur: heat is always likely to flow from a hot object to a cold one, but never likely to flow in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure $7.9.1$.

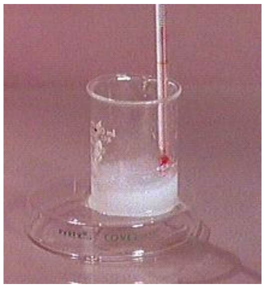


***Figure $7.9.1$:** An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see https://www.youtube.com/watch?v=GQkJI-Nq3Os.*

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "possibilities".

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the possible **arrangements** (sometimes called disorder, randomness, or freedom) of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular possibilities. The greater the number of atoms or molecules in the gas, the greater the possible arrangements. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure $7.9.2$. There are approximately 10^{68} (52!) different ways they might be arranged, which corresponds to 10^{68} different microscopic states. Card games assign a higher value to a hand that has a low degree of probability. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered (according to the rules of poker) and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

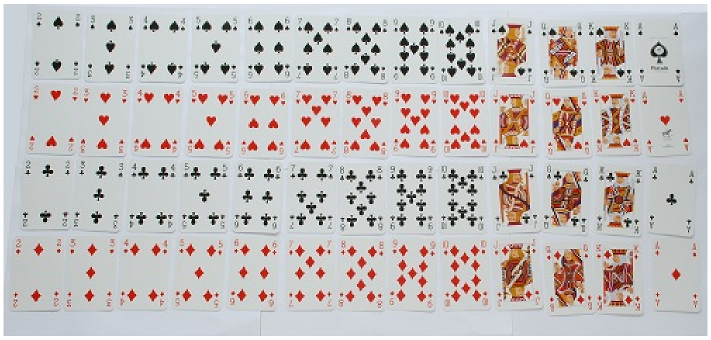


Figure $7.9.2$: *Illustrating High- and Low-Entropy States with a Deck of Playing Cards. A randomly shuffled deck of 52 cards can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. The deck above shows a single arrangement, and thus represents one of these microstates. If this is the sole, desired arrangement of cards, the arrangement has a very low entropy because there is only one possible way to obtain this arrangement (1 out of 52!). The card game of canasta uses 108 cards, and so a canasta deck has a higher number of possible microstates (108!), and could be said to have a higher entropy than a standard deck.*

Image used with permission (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure $7.9.3$). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure $7.9.3$, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter most often, with half the gas molecules in each bulb, is the most probable arrangement. The other states are not impossible but simply less likely.

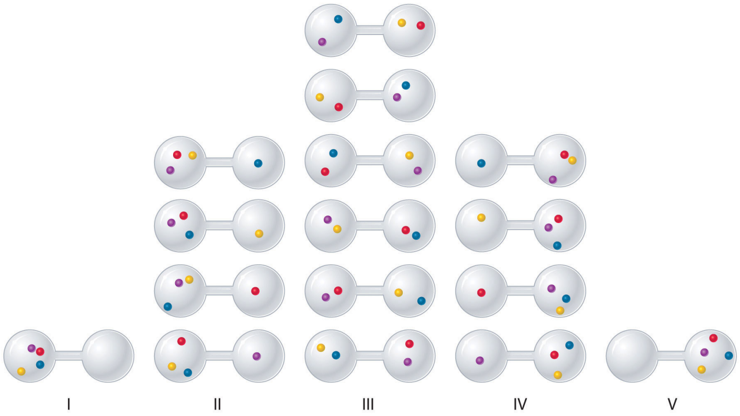


Figure 7.9.3: *The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume*

There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is least likely to be observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas which contains 2.69×10^{22} molecules. If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A system that has a large number of possible microstates because the particles are free to move has a high entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of possibilities. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 7.9.4, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

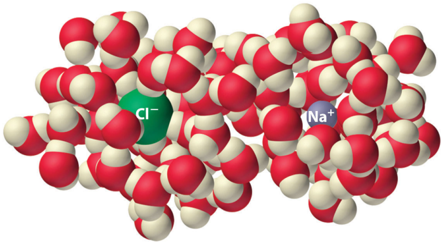


***Figure* 7.9.4:** *The Effect of Solution Formation on Entropy*

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

Example 7.9.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of NH_3(g) or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise 7.9.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm or a sample of 2 mol of NH_3(g) at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer a

a mixture of 3 mol of H_2(g) and 1 mol of N_2(g) at 25°C and 1 atm (more molecules of gas are present)

Video Solution

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an non-spontaneous process that is driven to occur by the addition of work to the system. The entropy of the universe will continue to increase until equilibrium is reached. Although we do not know what it means for the universe to be at equilibrium, we do know that there is no change in entropy for any chemical or physical process that is at equilibrium. Thus, equilibrium must be the most likely situation for any system. A system at equilibrium is likely to stay at equilibrium, and a system that is not at equilibrium is likely to change so that it can reach equilibrium. The most likely thing to happen does not have to happen, nor is it guaranteed to happen. Simply put, the most likely thing to happen is the most likely thing to happen.

As an example, consider the entropy changes that accompany the transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} = \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{7.9.1}$$

The numerators on the right side of Equation 7.9.1 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will (very likely) occur as written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will (very likely) occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 7.9.7).

***Figure 7.9.7**: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance*

Summary

A measure of the possible arrangements of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. For a given system, the greater the number of microstates, the higher the entropy. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that the entropy of a system at equilibrium is constant and does not have an effect on the entropy of the universe, whereas in a system that is not at equilibrium, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

Contributors

- Modified by Tom Neils (Grand Rapids Community College)

7.10: Gibbs Free Energy

Skills to Develop

- To understand the relationship between the standard Gibbs free energy change, the extent of reaction, and equilibrium
- To understand the relationship between Gibbs free energy change and the direction in which a reaction will proceed to reach equilibrium
- To understand the relationship between Gibbs free energy and work.

Gibbs Free-Energy

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{7.10.1}$$

Because it is a combination of state functions, G is also a state function.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe.

Standard Gibbs Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. This set of conditions required for determining ΔG° is rarely, if ever, encountered when carrying out chemical reactions, so the literal meaning of ΔG° is of questionable value. However, the **sign** and **magnitude** of ΔG° are extremely helpful in describing whether the reaction is product-favored or reactant-favored when it has reached equilibrium, which is sometimes known as the extent of a chemical reaction.

The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 7.10.2:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7.10.2}$$

- ΔG° < 0 means that the reaction is product-favored at equilibrium; the odds are in favor of making a significant amount of product at equilibrium.

- ΔG° > 0 means that the reaction is reactant-favored at equilibrium; the odds are against making a significant amount of product at equilibrium.

It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that, at equilibrium, the concentrations of the products will be less than the concentrations of the reactants.

- ΔG° = 0 means that the reaction is neither product-favored nor reactant-favored at equilibrium; there are 50:50 odds that a significant amount of product will be made at equilibrium.

This situation is rare for chemical reactions, although it can happen. This situation describes all phase changes when they occur at the exact phase change temperature.

Exercise 7.10.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction product-favored at equilibrium as written at 25°C?

Hint

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the standard entropy change (ΔS^o) is -0.332 kJ/(mol•K)

Answer

149.5 kJ/mol

no, not product-favored, but reactant-favored, at equilibrium

Video Solution

Calculated values of ΔG° are used to predict whether a reaction will be product-favored at equilibrium when the reactants and products are mixed under standard conditions. Very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG, notice the missing nought!) under the actual experimental conditions, which are usually quite different from ΔG°. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

We can also use the signs of ΔH° and ΔS° to determine the **sign** of ΔG° for a given reaction at various temperatures. Using Equation 7.10.2, the sign of ΔG° can be predicted for a reaction, using the signs of ΔH° and ΔS°:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7.10.3}$$

sign of ΔH°	sign of ΔS°	sign of ΔG°	Meaning
–	+	–	The reaction is product-favored at equilibrium at all temperatures; always likely; odds always favor it
+	–	+	The reaction is reactant-favored at equilibrium at all temperatures; never likely; odds are always against it
+	+	-/+	The **sign** of ΔG° is temperature dependent. The reaction will be product-favored at relatively **high** temperatures.
–	–	-/+	The **sign** of ΔG° is temperature dependent. The reaction will be product-favored at relatively **low** temperatures.

NOTE: If ΔS° and ΔH° for a reaction have the same sign, then the **sign** of ΔG° depends on the temperature and thus the relative magnitudes of the ΔH° and TΔS° terms.

If ΔS° and ΔH° for a reaction have the same sign, then there is a specific temperature at which the sign of ΔG° must equal 0 as the reaction shifts from being reactant-favored at equilibrium to being product-favored at equilibrium, and vice versa. The temperature at which this flip over occurs, at which a given reaction is neither product-favored nor reactant-favored, can be calculated by setting ΔG° = 0 in Equation 7.10.2, as illustrated in Example 7.10.2

Example 7.10.2

The reaction of nitrogen and hydrogen gas to produce ammonia

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(l).$$

is one in which ΔH° is −91.8 kJ and ΔS° is −198.1 J/K (both are negative). Such reactions are predicted to be product-favored at low temperatures but reactant-favored at high temperatures.

Calculate the temperature at which this reaction changes from product-favored to reactant-favored, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from product-favored to reactant-favored

Strategy:

Set ΔG° equal to zero in Equation 7.10.2and solve for T, the temperature at which the reaction becomes reactant-favored.

SOLUTION

The temperature at which the reaction becomes reactant-favored at equilibrium is found by setting ΔG° equal to zero and rearranging Equation 7.10.2to solve for T:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \\ T = \frac{\Delta H^\circ}{\Delta S^\circ} &= \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{-198.1 \text{ J/K}} = 463 \text{ K} \end{aligned}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 7.10.2

ΔH°= -116.2 kJ and ΔS° = - 146.6 J/K for the reaction of nitric oxide and oxygen to form nitrogen dioxide.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(l).$$

Use those data to calculate the temperature at which this reaction changes from product-favored to reactant-favored.

Answer

792.6 K

Video Solution

Gibbs Free Energy and the Direction of Spontaneous Reactions

A second major goal of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously, that is, if it will proceed in the forward direction, as written, to reach equilibrium. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will go in the forward direction as written to reach equilibrium. Conversely, if $\Delta S_{univ} < 0$, a process will go in the reverse direction as written to reach equilibrium; if $\Delta S_{univ} = 0$, the system is already at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the direction of a reaction as it proceeds towards equilibrium. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This calculation is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient, and is provided by the Gibbs free energy.

The criterion for predicting the likely direction for the reaction to occur to reach equilibrium is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{7.10.4}$$

where all thermodynamic quantities are those of the system.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 7.10.4 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995.

For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously, that is, it proceeds in the forward direction, as written, until it reaches equilibrium.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction, until it reaches equilibrium.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. The value of ΔS is $108.96\ \mathrm{J/K}$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\mathrm{C}} &= \Delta H_{100^\circ\mathrm{C}} - T\Delta S_{100^\circ\mathrm{C}}\\ &= 40{,}657\ \mathrm{J} - [(373.15\ \mathrm{K})(108.96\ \mathrm{J/K})]\\ &= 0\ \mathrm{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\mathrm{C}} &= \Delta H - T\Delta S\\ &= 40{,}657\ \mathrm{J} - [(383.15\ \mathrm{K})(108.96\ \mathrm{J/K})]\\ &= -1091\ \mathrm{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\mathrm{C}} &= \Delta H - T\Delta S\\ &= 40{,}657\ \mathrm{J} - [(363.15\ \mathrm{K})(108.96\ \mathrm{J/K})]\\ &= 1088\ \mathrm{J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ C}$ = 1090 J = $-\Delta G_{90^\circ C}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 7.10.2), setting $\Delta G = 0$, and solving for T,

$$0\text{ J}=40{,}657\text{ J}-T(108.96\text{ J/K})$$
$$T=373.15\text{ K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 7.10.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

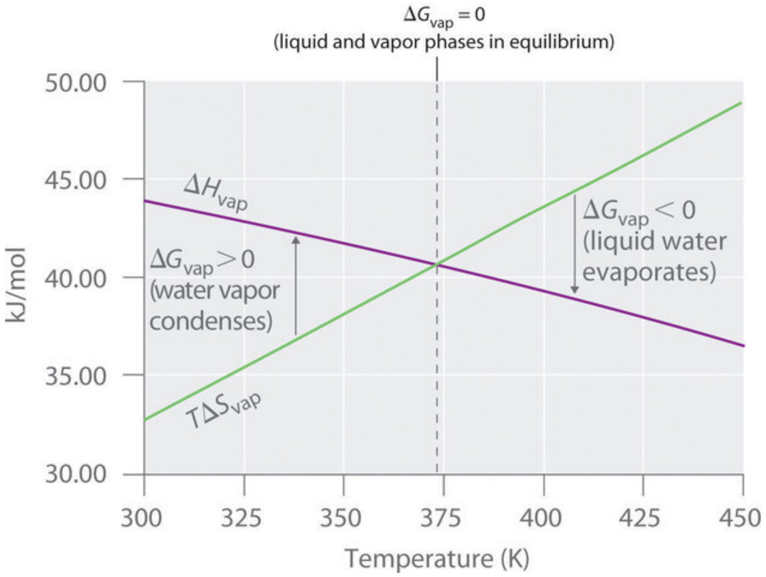


Figure 7.10.1: *Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.*

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the **magnitude** of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 7.10.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{7.10.5}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 7.10.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

***Table* 7.10.1:** *Approximate Thermodynamic Efficiencies of Various Devices*

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for describing two aspects of a reaction.
- Standard free-energy change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The sign of ΔG° tells us if a reaction will be reactant-favored (+ ΔG°) or product-favored (- ΔG°) at equilibrium. The magnitude of ΔG° tells us the extent of the reaction. A large +ΔG° tells us the reaction makes very little product at equilibrium. A large - ΔG° tells us the reaction makes a great deal of product at equilibrium.

- Free-energy change:

$$\Delta G = \Delta H - T\Delta S$$

The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written, but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change.

Contributors

Modified by Tom Neils (Grand Rapids Community College)

7.11 Gibbs Free Energy and Equilibrium

Skills to Develop

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously (that is, proceed in the forward direction, as written, to reach equilibrium): $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient Q versus the equilibrium constant K. Recall that if K > Q, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if K < Q, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If K = Q, then the system is at equilibrium, and no net reaction occurs. Table 1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

***Table 1**: Criteria for the Spontaneity of a Process as Written*

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
K > Q	K = Q	K < Q
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the free energy change of reaction (ΔG) and the instantaneous reaction quotient (Q). To do so, we will first reveal the relationship between the standard free energy change of a reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa.

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^{\circ} + RTlnQ = \Delta G^{\circ} + RT\ln Q \tag{1}$$

where ΔG° indicates that all reactants and products are in their standard states. For a system at equilibrium ($K = Q$,), and as you've learned in this chapter, ΔG = 0 for a system at equilibrium. Therefore, we can describe the relationship between ΔG° and K as follows:

$$0 = \Delta G^{\circ} + RT\ln K \tag{2}$$

$$\Delta G^{\circ} = -RT\ln K \tag{3}$$

If you combine equations 1 and 3, you get the equation

$$\Delta G = RT\ln\frac{Q}{K} \tag{4}$$

If the products and reactants are in their standard states and ΔG° < 0, then K > 1, and products are favored over reactants at equilibrium. Conversely, if ΔG° > 0, then K < 1, and reactants are favored over products at equilibrium. If ΔG° = 0, then $K = 1$, and neither reactants nor products are favored at equilibrium.

> *For a product-favored process under standard conditions, K is greater than 1.*

Example 1

Calculate K for the reaction of O_2 with N_2 to give NO at 423 K:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ΔG° for this reaction is +22.7 kJ/mol of N_2.

Given: ΔG°, and temperature

Asked for: K

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 3 to calculate K, the equilibrium constant for the formation of nitrogen monoxide.

SOLUTION

For equilibrium conditions, rearranging Equation 3,

$$\Delta G^{\circ} = -RT \ln K_{\mathrm{p}} \tag{5}$$

$$\frac{-\Delta G^{\circ}}{RT} = \ln K_{\mathrm{p}} \tag{6}$$

Inserting the value of ΔG° and the temperature (423 K) into this equation,

$$\ln K = -\frac{(-22.7\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(423\ \mathrm{K})} = -6.45 \tag{7}$$

$$K = 1.6 \times 10^{-3} \tag{8}$$

Thus the equilibrium constant for the formation of nitrogen monoxide at room temperature is less than 1. The reaction is reactant-favored at equilibrium.

Exercise 1

Calculate K for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is −70.5 kJ/mol of O_2.

Answer

2.2×10^{12}

Example 2

ΔG° is −32.7 kJ/mol of N_2 for the reaction at 100°C

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Calculate ΔG for the same reaction under the following nonstandard conditions:

- $[N_2]$ = 2.00 M,
- $[H_2]$ = 7.00 M,
- $[NH_3]$ = 0.021 M,
- and T = 100°C.

In which direction must the reaction proceed to reach equilibrium?

Given: balanced chemical equation, molarity of each species, temperature, and ΔG°

Asked for: the direction in which the reaction will proceed to reach equilibrium

Strategy:

A. Using the concentration values given, calculate Q.
B. Using the value of ΔG°, calculate the value of K using Equation 3
C. Substitute the values of K and Q into Equation 4 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A Using the equilibrium constant expression for the given reaction, we can calculate Q:

$$Q = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Using the value of ΔG°, calculate the value of K

$$\Delta G^o = -32,700J = -(8.314\frac{J}{g\cdot K})(373K)lnK \tag{9}$$

$$\frac{-32,700J}{-8.314\frac{J}{g\cdot K}\cdot 373K} = lnK \tag{10}$$

$$e^{10.54} = 38,000J = K \tag{11}$$

C Substituting the values of K and Q into Equation 1,

$$\Delta G = RTln\frac{Q}{K} = (8.314J/K)(373K)\left(\frac{1kJ}{1000J}\right)\ln\frac{6.4\times10^{-7}}{3.8\times10^4}$$

$$= -77\ \mathrm{kJ}_2$$

Because ΔG < 0 and K > Q, the reaction is spontaneous in the forward direction, as written. In other words, the reaction must proceed to the right to reach equilibrium.

Exercise 2

Calculate ΔG for the reaction $N_{2g} + O_{2(g)} \rightleftharpoons 2NO_g$ under the conditions: T = 423 K, $[NO]$ = 0.0100 M, $[O_2]$ = 0.200 M, and $[N_2]$ = 1.00 × 10^{-4} M. The value of ΔG° for this reaction is +22.7 kJ. In which direction will the reaction proceed to reach equilibrium?

Answer

ΔG = +28.3 kJ; the reaction is nonspontaneous to the right as written, so the reaction will go to the left to reach equilibrium. This can be verified by the fact that K < Q.

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 3, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{12}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 12 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 12 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 12 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{13}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{14}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{15}$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature.

Summary

Both K and ΔG° can be used to predict the ratio of products to reactants at equilibrium for a given reaction. ΔG° is related to K by the equation $\Delta G^\circ = -RT\ln K$.

- If ΔG° < 0, then K > 1, and products are favored over reactants at equilibrium.
- If ΔG° > 0, then K < 1, and reactants are favored over products at equilibrium.
- If ΔG° = 0, then K = 1, and the amount of products will be roughly equal to the amount of reactants at equilibrium. This is a rare occurrence for chemical reactions.

If a system is not at equilibrium, ΔG and Q can be used to tell us in which direction the reaction must proceed to reach equilibrium. ΔG is related to Q by the equation $\Delta G = RT\ln\frac{Q}{K}$.

- If ΔG < 0, then K > Q, and the reaction must proceed to the right to reach equilibrium.
- If ΔG > 0, then K < Q, and the reaction must proceed to the left to reach equilibrium.
- If ΔG = 0, then K = Q, and the reaction is at equilibrium.

We can use the measured equilibrium constant K at one temperature, along with ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors

- Mike Blaber (Florida State University)
- Modified by Tom Neils (Grand Rapids Community College)

What we are studying

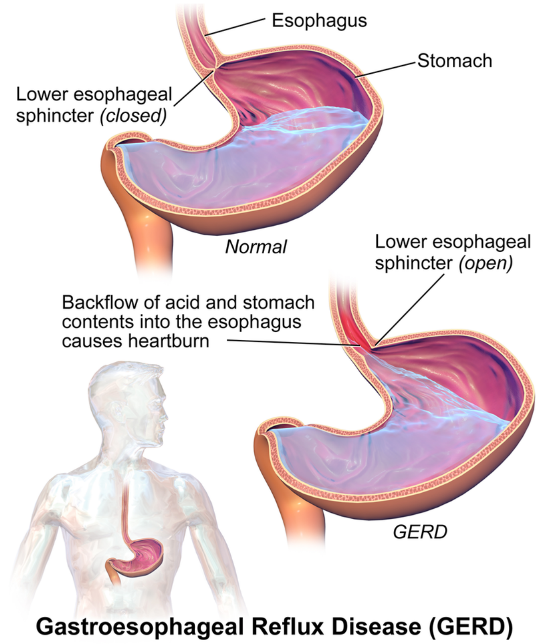
CHAPTER OVERVIEW

8: Acids and Bases

8.1: An Introduction to Acids and Bases

Why Do We Care about Acids and Bases?

Heartburn is caused by a buildup of excessive amounts of stomach acid, particularly HCl. This acid is used to digest the food we eat, but it can often back up into the esophagus causing that burning sensation many of us are familiar with. The symptoms of heartburn can be treated with a mild base, which acts to neutralize the excess HCl. For example, Tums is a very commonly used antacid that can be bought over the counter. Other antacids, such as Alka Seltzer, work in similar ways. Below is shown the reaction in which calcium carbonate (the active ingredient in Tums) neutralizes HCl in a simple proton transfer reaction. Following this acid-base reaction, carbonic acid quickly degrades into CO_2 and H_2O.



A comparison of a healthy condition to GERD. Image used with permission (Cc BY-SA 4.0; BruceBlaus .

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow H_2CO_{3(aq)} + CaCl_{2(aq)}$$
$$H_2CO_{3(aq)} \rightarrow H_2O_{(aq)} + CO_{2(g)}$$

General Descriptions of Acids and Bases

Acids and bases are common in many solutions that exist everywhere, and can be defined by their physical and chemical observations (Table 8.1.1).

***Table* 8.1.1**: *General Properties of Acids and Bases*

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).

ACIDS	BASES
have a pH<7 at 25^{o}C.	have a pH>7 at 25^{o}C.
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are *electrolytes*. Strong acids and bases will be strong **electrolytes**. Weak acids and bases will be weak electrolytes.

The Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An Arrhenius acid is a compound that increases the concentration of H^+ ions that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{8.1.1}$$

In this reaction, hydrochloric acid (HCl) dissociates into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{8.1.2}$$

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in acetone are not acidic, despite the fact that both of these acids will donate a proton to acetone. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definition can **only** describe acids and bases in an aqueous environment.

Contributors

- Anonymous
- Modified by Tom Neils (Grand Rapids Community College)

8.2: Brønsted-Lowry Acids and Bases

For all of the acid/base reactions, remember that the activity of water, as the solvent, is defined as 1.00. Therefore, the activity of water (sometimes mistakenly shown as [H_2O]) will not appear explicitly in any law of mass action equations (equilibrium constant expressions). The activity is **not** left out, it simply has a value of 1.00.

Learning Objectives

- 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

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). 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.

Previously, we defined acids and bases as Arrhenius did: An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions ($\mathrm{OH^-}$). This definition is not wrong; it is simply limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, $\mathrm{H^+}$. A proton is what remains when a normal hydrogen atom, $\mathrm{^1_1H}$, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid ($\mathrm{CH_3COOH}$) or ascorbic acid (vitamin C), or H_2O. Anions (such as $\mathrm{HSO_4^-}$, $\mathrm{H_2PO_4^-}$, $\mathrm{HS^-}$, and $\mathrm{HCO_3^-}$) and cations (such as $\mathrm{H_3O^+}$, $\mathrm{NH_4^+}$, and $\mathrm{[Al(H_2O)_6]^{3+}}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as $\mathrm{H_2O}$, $\mathrm{NH_3}$, and $\mathrm{CH_3NH_2}$), anions (such as $\mathrm{OH^-}$, $\mathrm{HS^-}$, $\mathrm{HCO_3^-}$, $\mathrm{CO_3^{2-}}$, $\mathrm{F^-}$, and $\mathrm{PO_4^{3-}}$), or cations (such as $\mathrm{[Al(H_2O)_5OH]^{2+}}$). The most familiar bases are ionic compounds such as NaOH and $\mathrm{Ca(OH)_2}$, which contain the hydroxide ion, $\mathrm{OH^-}$. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$\mathrm{H^+ + OH^- \rightarrow H_2O} \tag{8.2.1}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{8.2.2}$$

$$\mathrm{HF \rightleftharpoons H^+ + F^-} \tag{8.2.3}$$

$$\mathrm{H_2SO_4 \rightleftharpoons H^+ + HSO_4^-} \tag{8.2.4}$$

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-} \tag{8.2.5}$$

$$\mathrm{HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}} \tag{8.2.6}$$

$$\mathrm{NH_4^+ \rightleftharpoons H^+ + NH_3} \tag{8.2.7}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{8.2.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{8.2.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{8.2.10}$$

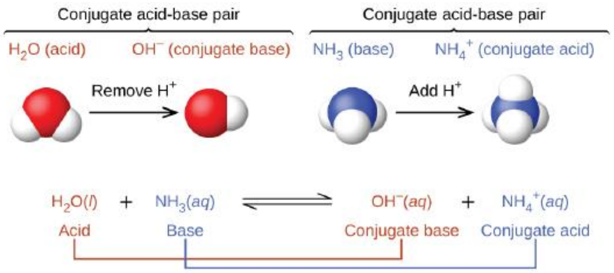
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{8.2.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{8.2.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{8.2.13}$$

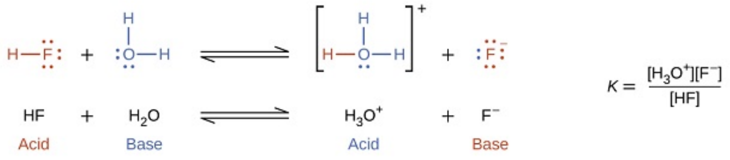
\[\ce{F^- +H^+ \rightleftharpoons HF} \label{16.2.3g} \]

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



A conjugate acid base pair if when we remove a H plus from the acid to get the conjugate base. Another conjugate acid base pair is when we add H plus to a base to get a conjugate acid. In a reaction: the acid and base are the reactants and the products are the conjugate base and conjugate 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:

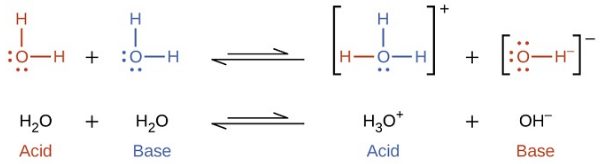


In this reaction HF is treated as the acid and water is treated as the base. The products as H3O plus and F minus. H3O plus is the acid and F minus is the base.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:

<div data-mt-source="1""This" height="167" width="612" src="/@api/deki/files/56740/CNX_Chem_14_01_NH3_img.jpg">

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



Here we have 2 water molecules reacting together. One water molecule is an acid while the second water molecule acts as a base. For the products, we get H3O plus and OH minus. H3O plus is the acid and OH minus is the base.

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O}_{(l)} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{H_3O}^+_{(aq)} + HO^-_{(aq)} \quad K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{8.2.14}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

A Video Discussing Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs [youtu.be]

✓ Example 8.2.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$. At 25 °C:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = [\mathrm{H_3O^+}]^{2+} = [\mathrm{OH^-}]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 8.2.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium determined by the autoionization reaction but it does shift the relative concentrations of $[OH-]$ and $[H_3O^+]$. Example 16.2.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw) [youtu.be]

Example 8.2.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 8.2.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[\mathrm{H_3O^+}] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO_{3(\mathit{aq})}^-} + \mathrm{H_2O_{(\mathit{l})}} \rightleftharpoons \mathrm{CO_{3(\mathit{aq})}^{2-}} + \mathrm{H_3O_{(\mathit{aq})}^+} \tag{8.2.15}$$

$$\mathrm{HCO_{3(\mathit{aq})}^-} + \mathrm{H_2O_{(\mathit{l})}} \rightleftharpoons \mathrm{H_2CO_{3(\mathit{aq})}} + \mathrm{OH_{(\mathit{aq})}^-} \tag{8.2.16}$$

Example 8.2.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $HSO_{3(aq)}^- + OH_{(aq)}^- \rightleftharpoons SO_{3(aq)}^{2-} + H_2O_{(l)}$
b. $HSO_{3(aq)}^- + HI_{(aq)} \rightleftharpoons H_2SO_{3(aq)} + I_{(aq)}^-$

Example 8.2.4

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer

a. $H_2PO_{4(aq)}^- + HBr_{(aq)} \rightleftharpoons H_3PO_{4(aq)} + Br_{(aq)}^-$
b. $H_2PO_{4(aq)}^- + OH_{(aq)}^- \rightleftharpoons HPO_{4(aq)}^{2-} + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes autoionization:

$$2\,\mathrm{H_2O_{(\mathit{l})}} \rightleftharpoons H_3O_{(aq)}^+ + OH_{(aq)}^-$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_\mathrm{w} = [\mathrm{H_2O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25^\circ\mathrm{C}$$

Key Equations

- $$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic

species that may either gain or lose a proton in a reaction

amphoteric

species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid

proton donor

Brønsted-Lowry base

proton acceptor

conjugate acid

substance formed when a base gains a proton

conjugate base

substance formed when an acid loses a proton

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

Contributors and Attributions

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

Modified by Tom Neils (Grand Rapids Community College)

8.3 Lewis Acids and Bases

Skills to Develop

- Understand that there is a more comprehensive theory of acid-base chemistry, called the Lewis concept, that describes acid-base reactions as the sharing of electron pairs.

The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

We will discuss Lewis acids and bases in more detail at the end of the chapter.

Contributors

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Modified by Tom Neils (Grand Rapids Community College)

8.4: Acid Strength and the Acid Dissociation Constant (Ka)

Skills to Develop

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{8.4.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{8.4.2}$$

As we noted earlier, the equilibrium constant expression (Law of Mass Action) is really a ratio of activities. The activities of the solutes can be replaced with their molar concentration without too much error if the solutions are dilute enough. However, the activity of water is essentially constant for all reactions in dilute aqueous solutions, and is assigned the value of "1" by definition. Thus, the $[H_2O]$ in Equation 8.4.2 is actually a misapplication of the approximation carried out for solutes. The proper sequence of approximations and substitutions is

$$K = K_a = \frac{(a_{H_3O^+})(a_{A^-})}{(a_{HA})(a_{H_2O})} \approx \frac{[H_3O^+][A^-]}{[HA][1]} = \frac{[H_3O^+][A^-]}{[HA]} \tag{8.4.3}$$

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 8.4.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. As with all equilibrium constants, acid–base ionization constants are unitless because each of the activities is divided by the standard activity with the same units . The values of K_a for a number of common acids are given in Table 8.4.1.

Table 8.4.1: *Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)*

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{8.4.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K = K_b = \frac{[BH^+][OH^-]}{[B]} \tag{8.4.5}$$

Once again, the activity of water is defined as a value of "1" because it is the solvent. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table $8.4.2$.

Table $8.4.2$: *Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)*

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00

*As in Table 8.4.1.

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)} \tag{8.4.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{8.4.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} \tag{8.4.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{8.4.9}$$

If we add Equations 8.4.6 and 8.4.7, we obtain the following:

Reaction	Equilibrium Constants
$H_2O_{(l)} + \cancel{HCN_{(aq)}} \rightleftharpoons H_3O^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H_3O^+] \cancel{[CN^-]} / \cancel{[HCN]}$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-] \cancel{[HCN]} / \cancel{[CN^-]}$
$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H_3O^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_a K_b = K_w \tag{8.4.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

We can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{8.4.11}$$

$$K_a = 10^{-pK_a} \tag{8.4.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{8.4.13}$$

$$K_b = 10^{-pK_b} \tag{8.4.14}$$

Similarly, Equation 8.4.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{8.4.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{8.4.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables $8.4.1$ and $8.4.2$, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

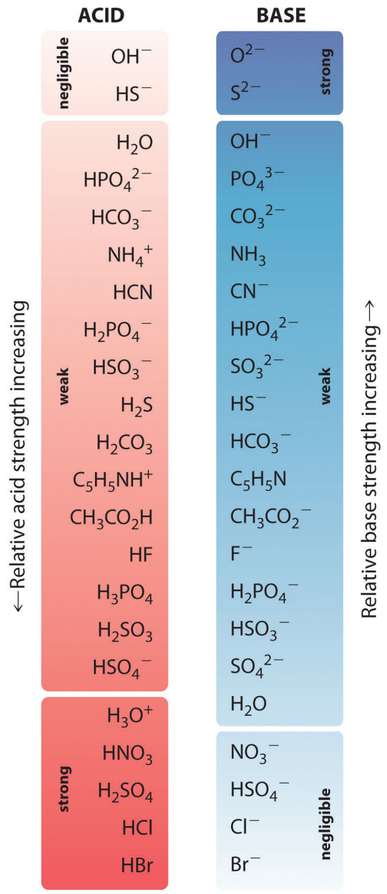


Figure $8.4.1$: *The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak* base, and, conversely, the conjugate acid of a strong base is a very weak acid.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure $8.4.1$. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure $8.4.2$ are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base} \tag{8.4.17}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{8.4.18}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO^-_{2\,(aq)}} \tag{8.4.19}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{8.4.20}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 8.4.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 8.4.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 8.4.15 and 8.4.16. Use the relationships pK = −log K and K = $10^{-\mathrm{pK}}$ (Equations 8.4.11 and 8.4.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 8.4.16: pK_a + pK_b = $\mathrm{pK_w}$ = 14.00. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00 \tag{8.4.21}$$

$$pK_b = 14.00 - 4.83 = 9.17 \tag{8.4.22}$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 8.4.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14} \tag{8.4.23}$$

$$K_a = 1.9 \times 10^{-11} \tag{8.4.24}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27 \tag{8.4.25}$$

$$pKa + pK_b = 14.00 \tag{8.4.26}$$

$$pK_a = 10.73 \tag{8.4.27}$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11} \tag{8.4.28}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 8.4.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer:

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table $8.4.1$ that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table $8.4.1$ were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table $8.4.2$, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{8.4.29}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{8.4.30}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{8.4.31}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2 \tag{8.4.32}$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO^{2-}_{4(aq)} + H_2O_{(aq)} \rightleftharpoons HSO^-_{4(aq)} + OH^-_{(aq)} \tag{8.4.33}$$

$$HSO^-_{4(aq)} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH^-_{(aq)} \tag{8.4.34}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by pK_a + pK_b = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table $8.4.1$, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 8.4.34 lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

Example 8.4.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH^+_{4(aq)} + PO^{3-}_{4(aq)} \rightleftharpoons NH_{3(aq)} + HPO^{2-}_{4(aq)}$
- $CH_3CH_2CO_2H_{(aq)} + CN^-_{(aq)} \rightleftharpoons CH_3CH_2CO^-_{2(aq)} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables $8.4.1 and 8.4.2$ and Figure $8.4.2$ to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables $8.4.1$ and $8.4.2$, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH^+_{4(aq)}} + \underset{\text{stronger base}}{PO^{3-}_{4(aq)}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO^{2-}_{4(aq)}} \tag{8.4.35}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table $8.4.1$, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table $8.4.1$, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-\mathrm{CH_2CH_3}$ versus $-\mathrm{CH_3}$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN^-_{(aq)}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO^-_{2(aq)}} + \underset{\text{weaker acid}}{HCN_{(aq)}} \tag{8.4.36}$$

Exercise 8.4.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

a. $H_2O_{(l)} + HS^-_{(aq)} \rightleftharpoons OH^-_{(aq)} + H_2S_{(aq)}$
b. $HCO^-_{2(aq)} + HSO^-_{4(aq)} \rightleftharpoons HCO_2H_{(aq)} + SO^{2-}_{4(aq)}$

Answer a

left

Answer b

left

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{8.4.37}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{8.4.38}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w \tag{8.4.39}$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a \tag{8.4.40}$$

$$K_a = 10^{-pK_a} \tag{8.4.41}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b \tag{8.4.42}$$

$$K_b = 10^{-pK_b} \tag{8.4.43}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w \tag{8.4.44}$$

$$pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C} \tag{8.4.45}$$

Contributors

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Modified by Tom Neils (Grand Rapids Community College)

8.5: Autoionization of Water and pH

Skills to Develop

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

As you learned previously acids and bases can be defined in several different ways (Table 8.5.1). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can donate a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can accept a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve two conjugate acid–base pairs and the transfer of a proton from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, focuses on accepting or donating pairs of electrons rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table* 8.5.1*: *Definitions of Acids and Bases*

Definition	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in aqueous solution, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{acid}{HCl_{(aq)}} + \underset{base}{H_2O_{(l)}} \rightarrow \underset{acid}{H_3O^+_{(aq)}} + \underset{base}{Cl^-_{(aq)}} \tag{8.5.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 8.5.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{8.5.2}$$

In Equation 8.5.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} \tag{8.5.3}$$

Water can also act as an acid, as shown in Equation 8.5.4. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{acid}{H_2O_{(aq)}} + \underset{base}{NH_{3(aq)}} \rightleftharpoons \underset{acid}{NH^+_{4(aq)}} + \underset{base}{OH^-_{(aq)}} \tag{8.5.4}$$

Water is thus termed amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 8.5.4 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Relationship among pH, pOH, and pK_w

As mentioned on a previous page, water can undergo the self-ionization reaction called autoprotolysis:

$$H_2O_{(l)} \; + \; H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction is

$$K_w = [H_3O^+][OH^-] = 1.0x10^{-14} \; at \; 25^oC \tag{8.5.5}$$

Thus, at 25 ^{o}C, for pure water, the [H_3O^+] = [OH^-] = 1.0 x 10^{-7}M. If a substance is added to water so that the [H_3O^+] > [OH^-], the solution is considered acidic. If a substance is added to water so that the [H_3O^+] < [OH^-], the solution is considered basic. This is a perfectly reasonable set of relationships to use to decide if a solution is acidic or basic. However, scientists in the early 1900's decided to add a second set of relationships to describe the acidity of a solution, using logarithms to convert the small [H_3O^+] and [OH^-] concentrations to a more 'manageable' number. This second set of relationships involves the calculation of pH and pOH values, where pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[H^+] \tag{8.5.6}$$

$$[H^+] = 10^{-pH} \tag{8.5.7}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Using the pH scale, the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7} \; M$), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -\log_{10}[OH^-] \tag{8.5.8}$$

$$[OH^-] = 10^{-pOH} \tag{8.5.9}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log \; K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25 °C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25 °C by taking the negative logarithm of both sides of Equation 8.5.5:

$$-\log_{10} K_w = pK_w \tag{8.5.10}$$

$$= -\log([H_3O^+][OH^-]) \tag{8.5.11}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{8.5.12}$$

$$= pH + pOH \tag{8.5.13}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25 °C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 8.5.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

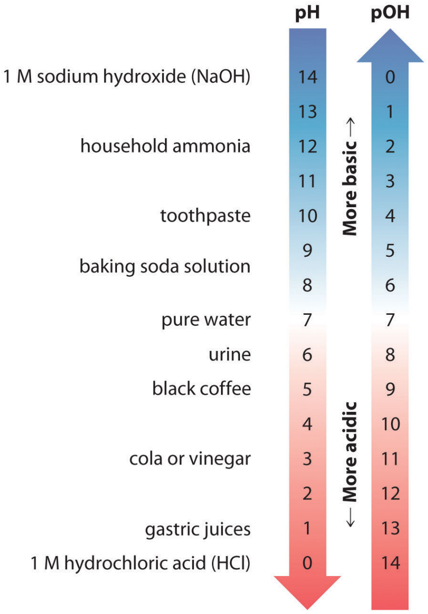


***Figure* $8.5.1$** *: The Inverse Relationship between the pH and pOH Scales. As pH decreases,* $[H^+]$ *and the acidity increase. As pOH increases,* $[OH^-]$ *and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.*

> *For any neutral solution, pH + pOH = 14.00 (at 25 °C) with pH=pOH=7.*

Example $8.5.1$

The K_w for water at 100 °C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100 °C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pK_w by taking the negative logarithm of K_w.
B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 8.5.5 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A

Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302 \tag{8.5.14}$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B

Equation 8.5.5 shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned}K_w &= [H_3O^+][OH^-] \\ &= (x)(x) = x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M\end{aligned}$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\begin{aligned}pH &= pOH = -\log(7.06 \times 10^{-7}) \\ &= 6.15 \ \text{(to two decimal places)}\end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 8.5.13, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can set $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$\begin{aligned}pK_w &= pH + pOH \\ &= y + y \\ &= 2y \\ y &= \frac{pK_w}{2} \\ &= \frac{12.302}{2} \\ &= 6.15 = pH = pOH\end{aligned}$$

Exercise 8.5.1

Humans maintain an internal temperature of about 37 °C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37 °C. Report pH and pOH values to two decimal places.

Answer

- $pK_w = 13.45$
- $pH = pOH = 6.73$

Summary

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (Kw) and is defined as $K_w = [H_3O^+][OH^-]$. At 25 °C, K_w is 1.0×10^{-14}; hence $pH + pOH = pK_w = 14.00$.

- For any neutral solution, $pH + pOH = 14.00$ (at 25 °C) and $pH = 1/2 pK_w$.
- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log 10[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^-]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

Contributors

Modified by Tom Neils (Grand Rapids Community College)

8.6 - Finding the Hydronium Ion Concentration and pH of Strong and Weak Acid Solutions

If we wish to find the hydronium ion concentration ([H_3O^+]) and the pH of a solution, we need to know both the strength of the acid (or base) and the concentration of the acid (or base). We will find that we need to treat strong acids (and bases) differently than weak acids (and bases) based on the extent to which they react with water.

Strong Acids

By definition, strong acids are those acids with a $K_a \geq 1$. using this definition, we assume that strong acids will react completely with water, so that every molecule of acid reacts with a molecule of water to produce a hydronium ion and the conjugate base. (This assumption is, of course, not possible because there must always be at least a few particles of each reactant and each product at equilibrium, but our assumption is a valid one when K_a gets to be quite a bit larger than 1.):

$$HA_{(aq)}\ +\ H_2O_{(l)} \rightarrow H_3O^+_{(aq)}\ +\ A^-_{(aq)} \tag{1}$$

Based on our assumption, $[H_3O^+]_{eq} = [HA]_{initial}$, so we can carry out the following calculation:

$$pH = -log([H_3O^+]_{eq}) = -log([HA]_{initial}) \tag{2}$$

Example 1

What is the pH of a 0.175 M aqueous solution of HBr?

Solution

HBr is a strong acid ($K_a > 1$), so $[H_3O^+]_{eq} = [HBr]_{initial}$. Thus, pH = -log (0.175) = 0.757

Exercise 1

What is the pH of a 0.0043 M aqueous solution of HNO_3?

Answer

HNO_3 is a strong acid ($K_a > 1$), so $[H_3O^+]_{eq} = [HNO_3]_{initial}$. Thus, pH = -log (0.0043) = 2.37

Strong Bases

By definition, strong bases are those bases with a $K_b \geq 1$. using this definition, we assume that strong bases will react completely with water, so that every molecule of base reacts with a molecule of water to produce a hydroxide ion and the conjugate acid. (This assumption is, of course, not possible because there must always be at least a few particles of each reactant and each product at equilibrium, but our assumption is a valid one when K_b gets to be quite a bit larger than 1.):

$$B_{(aq)}\ +\ H_2O_{(l)} \rightarrow OH^-_{(aq)}\ +\ HB^+_{(aq)} \tag{3}$$

Based on our assumption, $[OH^-]_{eq} = [B]_{initial}$, so we can carry out the following calculation:

$$pOH = -log([OH^-]_{eq}) = -log([B]_{initial}) \tag{4}$$

To find the pH, we then subtract the pOH from 14.

Example 2

What is the pH of a 0.175 M aqueous solution of $NaNH_2$?

Solution

NH_2^- is a strong base ($K_b > 1$), so $[OH^-]_{eq} = [NH_2^-]_{initial}$. Thus, pOH = -log (0.175) = 0.757, and pH = 14.000 - 0.757 = 13.243

Exercise 2

What is the pH of a 0.0043 M aqueous solution of KOH?

Answer

KOH is a strong base ($K_b = 1$), so $[OH^-]_{eq} = [OH^-]_{initial}$. Thus, pOH = -log (0.0043) = 2.37, and pH = 14.00 - 2.37 = 11.63

Weak Acids

If the acid you are working with is weak ($K_a < 1$), you must use a logic chart (ICE diagram) to determine the $[H_3O^+]$ because you cannot tell how much H_3O^+ will form in solution simply by looking at the intial $[HA]$.

Example 3

What is the pH of a 0.025 M aqueous solution of HClO?

Solution

ClO^- is a weak base with $K_b = 3.5\ x\ 10^{-8}$. The law of mass action for the reaction of $HClO$ with water is $3.5\ x\ 10^{-8} = \frac{[ClO^-][H_3O^+]}{[HClO]}$

The ICE diagram will look like this:

HClO	H_2O	⇌	ClO^-	H_3O^+
0.025	-		0	0
-n	-		+n	+n
0.025-n	-		n	n

Thus,

$$3.5\ x\ 10^{-8} = \frac{[n][n]}{[0.025 - n]} \tag{5}$$

which rearranges to

$$0 = n^2 + 3.5\ x\ 10^{-8} n - 8.75\ x\ 10^{-10} \tag{6}$$

using the quadratic formula, the answer can be found to be 2.96 x 10^{-5} M H_3O+. Thus the pH is -log(2.96 x 10^{-5}) = 4.53

Exercise 3

What is the pH of a 0.111 M aqueous solution of acetic acid? $K_a = 1.8 \times 10^{-5}$

Answer

pH = 2.85

Weak Bases

If the base you are working with is weak ($K_b < 1$), you must use a logic chart (ICE diagram) to determine the $[OH^-]$ because you cannot tell how much OH^- will form in solution simply by looking at the intial $[B]$.

Example 4

What is the pH of a 0.025 M aqueous solution of NaClO?

Solution

ClO^- is a weak base with $K_b = 2.9\ x\ 10^{-7}$. The law of mass action for the reaction of ClO^- with water is $2.9\ x\ 10^{-7} = \frac{[HClO][OH^-]}{[ClO^-]}$

The ICE diagram will look like this:

ClO^-	H_2O	⇌	HClO	OH^-
0.025	-		0	0
-n	-		+n	+n
0.025-n	-		n	n

Thus,

$$2.9\ x\ 10^{-7} = \frac{[n][n]}{[0.025 - n]} \tag{7}$$

which rearranges to

$$0 = n^2 + 2.9\ x\ 10^{-7} n - 7.25\ x\ 10^{-9} \tag{8}$$

using the quadratic formula, the answer can be found to be 2.68 x 10^{-5} M OH^-. Thus the pOH is -log(2.68 x 10^{-5}) = 4.57, and the pH is 14.00 -4.57 = 9.43.

Exercise 4

What is the pH of a 0.045 M aqueous solution of sodium phosphate. $K_b = 2.8 \times 10^{-2}$

Answer

12.38

Contributor

- Tom Neils (Grand Rapids Community College)

8.7: The Acid-Base Properties of Ions and Salts

Skills to Develop

- To understand hydrolysis
- To predict the effect a given ion will have on the pH of a solution

Depending on the acid–base properties of its component ions, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a **very** weak acid (K_a < 1 x 10^{-14}) . The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character (K_b < 1 x 10^{-14}). Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively and they have K_a > 1 x 10^{-14}.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)} \tag{8.7.1}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)} \tag{8.7.2}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table $8.7.1$ and Figure $8.7.1$, we can see that CN^- is a stronger base ($pK_b = 4.79$) than acetate ($pK_b = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Equation 8.7.3). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water because they have a K_b > 1 x 10^{-14}. The reactions are as follows:

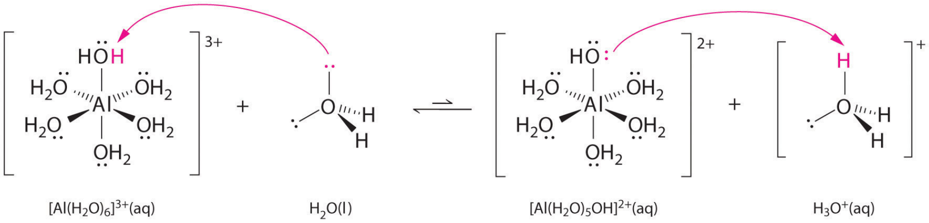
$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{8.7.3}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{8.7.4}$$

Equation 8.7.3 indicates that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation and the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Equation 8.7.4, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base (Ka ≈ Kb). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the cation is a stronger acid than the anion is a base, the final solution has a pH < 7.00. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a pH > 7.00.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure $8.7.1$). A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.



Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the $\mathrm{O-H}$ bonds, as shown in part (b) in Figure $8.7.1$. With less electron density between the O atoms and the H atoms, the $\mathrm{O-H}$ bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

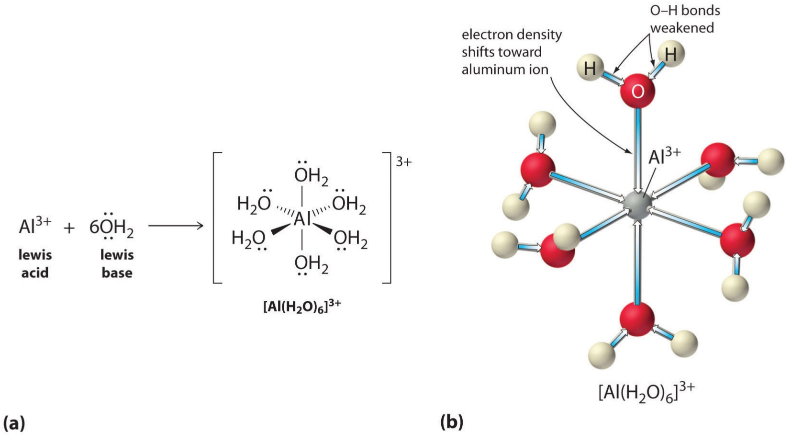


Figure $8.7.1$: *Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.*

The magnitude of this effect depends on the following two factors (Figure $8.7.2$):

1. The charge on the metal ion. A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.
2. The radius of the metal ion. For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

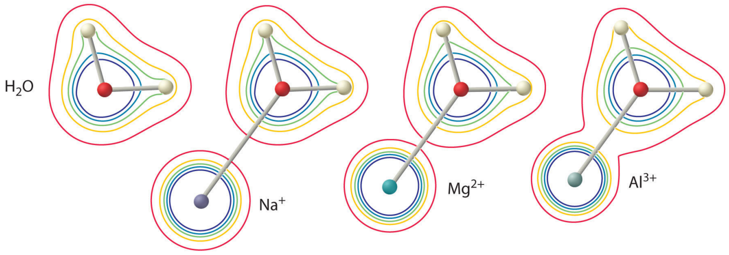


Figure $8.7.2$: *The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.*

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{8.7.5}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the charge-to-radius ratio of the metal ion.

> *Solutions of small, highly charged metal ions in water are acidic.*

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

> *A hydrolysis reaction is an acid–base reaction.*

Example 8.7.1

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

a. KNO_3
b. $CrBr_3$
c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A. Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.
B. f the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a

A. The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so its $K_a < 1 \times 10^{-14}$. It will not hydrolyze water or affect the pH.
B. The NO_3- anion is the conjugate base of a strong acid, so it has essentially no basic character ($K_b < 1 \times 10^{-14}$).
C. Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

b.

A. The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[Cr(H2O)_6]^{3+}$ complex, which will behave as a weak acid:

$$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)}$$

   ($K_a > 1 \times 10^{-14}$)
B. The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution ($K_b < 1 \times 10^{-14}$).
C. Hence the solution will be acidic.

c.

A. The Na^+ ion, like the K^+, is a very weak acid ($K_a < 1 \times 10^{-14}$), so it should not affect the acidity of the solution.
B. In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion, with a $K_b > 1 \times 10^{-14}$, will react with water as shown in Figure 16.6.
C. The solution will be slightly basic.

Exercise 8.7.1

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

a. KI
b. $Fe(ClO_4)_2$
c. $NaHS$

Answer a

neutral

Answer b

acidic

Answer c

basic (due to the reaction of HS^- with water to form H_2S and OH^-)

Summary

A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a hydrolysis reaction.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

Contributors

Modified by Tom Neils (Grand Rapids Community College)

8.8: Buffers: Solutions That Resist pH Change

Skills to Develop

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or “buffer,” other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect with Acids and Bases

To understand how buffers work, let’s look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier’s principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO^-(aq) + H^+(aq) \tag{8.8.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3CO_2]}{[CH_3CO_2H]} \tag{8.8.2}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier’s principle predicts that the equilibrium in Equation 8.8.1 will shift to the left, consuming some of the added $CH_3CO_2^-$ and some of the H^+ ions originally present in solution.

Because Na^+ is a *spectator ion*, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

Now let’s suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \tag{8.8.3}$$

If the equilibrium constant for the reaction as written in Equation 8.8.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 8.8.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier’s principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0 – 5.0 = 9.0. \tag{8.8.4}$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{8.8.5}$$

Again, the equilibrium constant for the reverse of this reaction is very large: K = 1/K_a = 10^9. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 8.8.5 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

The buffer acid will always react with any added (intruder) base such as OH^-, to remove that OH^-. The net result of the reaction is that water is produced and the ratio of $\frac{[buffer\ base]}{[buffer\ acid]}$ is **increased**:

$$BH^+(aq) + OH^-(aq) \rightleftharpoons B(aq) + H_2O(l) \tag{8.8.6}$$

The buffer base will always react with any added (intruder) acid such as H_3O^+, to remove that H_3O^+. The net result of the reaction is that water is produced and the ratio of $\frac{[buffer\ base]}{[buffer\ acid]}$ is **decreased**:

$$B(aq) + H_3O^+(aq) \rightleftharpoons BH^+(aq) + H_2O(l) \tag{8.8.7}$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure 8.8.1 illustrates both actions of a buffer made from the conjugate pair HAn/An^-.

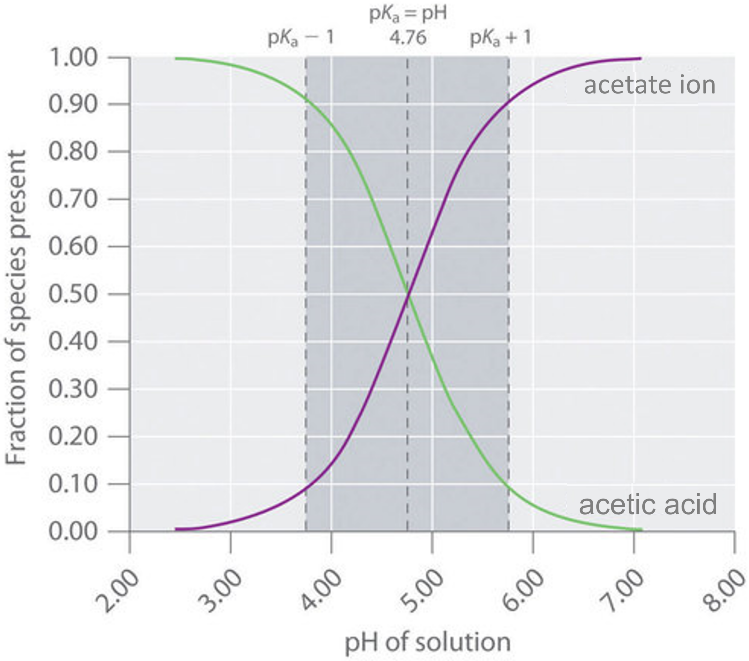


***Figure 8.8.1**: The Actions of Buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.*

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 8.8.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{8.8.8}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{8.8.9}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{8.8.10}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{8.8.11}$$

Replacing the negative logarithms in Equation 8.8.11,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{8.8.12}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{8.8.13}$$

Equation 8.8.12 and Equation 8.8.13 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1 \tag{8.8.14}$$

  in Equation 8.8.13. Because $\log 1 = 0$,

  $$pH = pK_a \tag{8.8.15}$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 8.8.13, because $\log 10 = 1$,

  $$pH = pK_a + 1. \tag{8.8.16}$$

- $[base]/[acid] = 100$: In Equation 8.8.13, because $\log 100 = 2$,

  $$pH = pK_a + 2. \tag{8.8.17}$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 8.8.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equation 8.8.12 or Equation 8.8.13) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 8.8.12), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]). \tag{8.8.18}$$

A

Inserting the given values into the equation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the [A$^-$]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 8.8.13, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\,M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w. \tag{8.8.19}$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

[

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$= 5.23 + \log\left(\frac{0.119}{0.234}\right)$$

$$= 5.23 \; - 0.294$$

$$= 4.94$$

\]

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise 8.8.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68

The Henderson-Hasselbalch approximation ((Equation 8.8.12) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example $8.8.3$.

Example 8.8.3

The buffer solution in Example $8.8.2$ contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example $8.8.1$. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 8.8.13) to obtain the pH.

Solution:

The added HCl (a strong acid) or $NaOH$ (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$HCO^{2-}(aq)+H^+(aq) \rightarrow HCO_2H(aq) \tag{8.8.20}$$

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	16.5 mmol	∼0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "∼0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 8.8.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \tag{8.8.21}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) = 3.75\ - 0.050 = 3.70 \tag{8.8.22}$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a − 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$HCO_2H(aq)+OH^-(aq) \rightarrow HCO_2^-(aq)+H_2O(l) \tag{8.8.23}$$

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	8.5 mmol	∼0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) = 3.75 + 0.494 = 4.24 \tag{8.8.24}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

Exercise 8.8.3

The buffer solution from Example 8.8.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M $NaOH$ are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a

5.30

Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.

The results obtained in Example 8.8.3 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

> *The most effective buffers contain equal concentrations of an acid and its conjugate base.*

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 8.8.2 for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

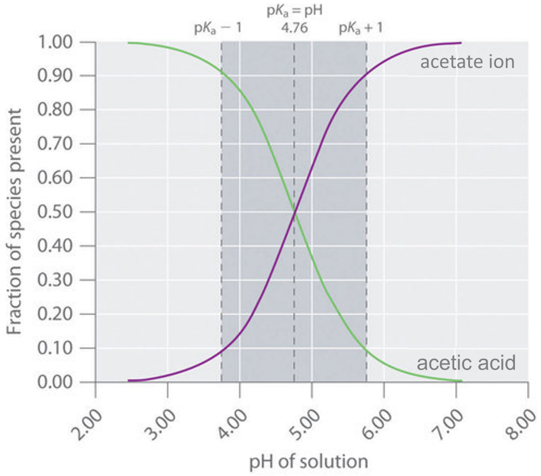


***Figure 8.8.2**: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to* $pH = pK_a \pm 1$ *).*

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_3(aq) \leftrightharpoons H^+(aq) + HCO_3^-(aq) \tag{8.8.25}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 8.8.25 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 8.8.25 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C. As shown in Equation 8.8.26, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$CO_2(aq) + H_2O(l) \leftrightharpoons H_2CO_3(aq) \tag{8.8.26}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 8.8.25 suggests. Adding Equation 8.8.26 and Equation 8.8.25 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_2(aq) + H_2O(l) \leftrightharpoons H_2CO_3(aq) \ (8.8.26)$$

with $K' = 4.0 \times 10^{-3} (37^\circ C)$

$$H_2CO_3(aq) \leftrightharpoons H^+(aq) + HCO_3^-(aq) \ (8.8.25)$$

with $K_a = 2.0 \times 10^{-4} (37^\circ C)$

$$CO_2(aq) + H_2O(l) \leftrightharpoons H^+(aq) + HCO_3^-(aq) \tag{8.8.27}$$

with $K = 8.0 \times 10^{-7} (37^\circ C)$

The K value for the reaction in Equation 8.8.27 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{8.8.28}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to **Henry's law**,

$$[CO_2] = kP_{CO_2} \tag{8.8.29}$$

where k is the Henry's law constant for CO_2, which is $3.0 \times 10^{-5}\ M/mmHg$ at 37°C. Substituting this expression for $[CO_2]$ in Equation 8.8.28,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})} \tag{8.8.30}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{8.8.31}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 8.8.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

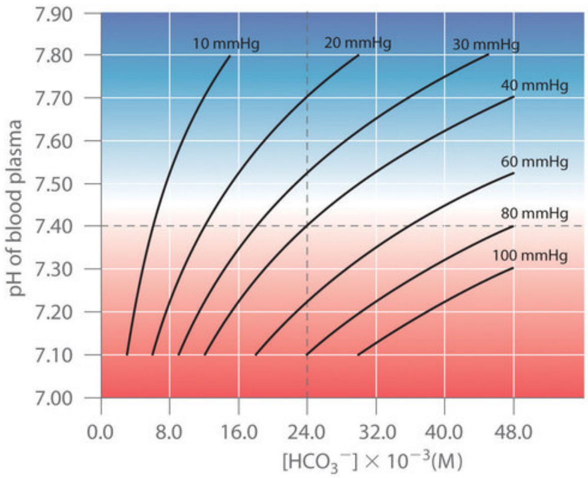


Figure 8.8.4: *Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines.*

According to Equation 8.8.27, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, Equation 8.8.31 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO2 to form $[HCO_3^-]$, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The CO_2/HCO_3^- buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

8.9 Buffer Capacity and Buffer Range

Buffer Capacity

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

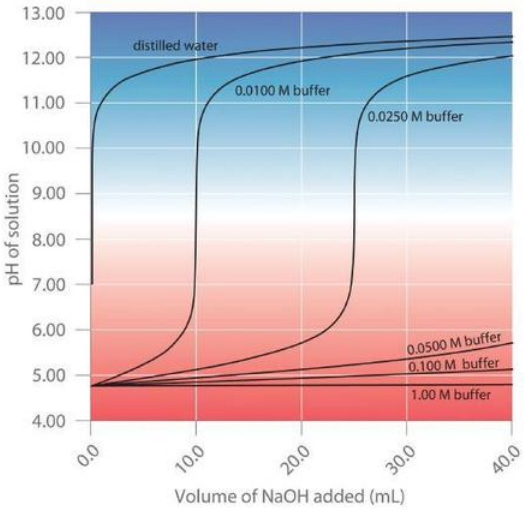


Figure* 1*: *Effect of Buffer Concentration on the Capacity of a Buffer*

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Selecting proper components for desired pH

Buffers function best when the pK_a of the conjugate weak acid used is close to the desired working range of the buffer. This turns out to be the case when the concentrations of the conjugate acid and conjugate base are approximately equal (within about a factor of 10). For example, we know the K_a for hydroflouric acid is 6.6 x 10^{-4} so its pK_a= -log(6.6 x 10^{-4}) = 3.18. So, a hydrofluoric acid buffer would work best in a buffer range of around pH = 3.18.

For the weak base ammonia (NH_3), the value of K_b is $1.8x10^{-5}$, implying that the K_a for the dissociation of its conjugate acid, NH_4^+, is $K_w/K_b=10^{-14}/1.8x10^{-5} = 5.6x10^{-10}$. Thus, the pK_a for NH_4^+ = 9.25, so buffers using NH_4^+/NH_3 will work best around a pH of 9.25. (It's always the pK_a of the conjugate acid that determines the approximate pH for a buffer system, though this is dependent on the pK_b of the conjugate base, obviously.)

When the desired pH of a buffer solution is near the pK_a of the conjugate acid being used (i.e., when the amounts of conjugate acid and conjugate base in solution are within about a factor of 10 of each other), the Henderson-Hasselbalch equation can be applied as a simple approximation of the solution pH, as we will see in the next section.

Example 1: HF Buffer

In this example we will continue to use the hydrofluoric acid buffer. We will discuss the process for preparing a buffer of HF at a pH of 3.0. We can use the Henderson-Hasselbalch approximation to calculate the necessary ratio of F^- and HF.

$$pH = pKa + \log \frac{[Base]}{[Acid]} \tag{1}$$

$$3.0 = 3.18 + \log \frac{[Base]}{[Acid]} \tag{2}$$

$$\log \frac{[Base]}{[Acid]} = -0.18 \tag{3}$$

$$\frac{[Base]}{[Acid]} = 10^{-0.18} \tag{4}$$

$$\frac{[Base]}{[Acid]} = 0.66 \tag{5}$$

This is simply the ratio of the concentrations of conjugate base and conjugate acid we will need in our solution. However, what if we have 100 ml of 1 M HF and we want to prepare a buffer using NaF? How much Sodium Fluoride would we need to add in order to create a buffer at said pH (3.0)?

We know from our Henderson-Hasselbalch calculation that the ratio of our base/acid should be equal to 0.66. From a table of molar masses, such as a periodic table, we can calculate the molar mass of NaF to be equal to 41.99 g/mol. HF is a weak acid with a K_a = 6.6 x 10^{-4} and the concentration of HF is given above as 1 M. Using this information, we can calculate the amount of F^- we need to add.

The dissociation reaction is:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons F^-_{(aq)} + H_3O^+_{(aq)} \tag{6}$$

We could use ICE tables to calculate the concentration of F^- from HF dissociation, but, since K_a is so small, we can approximate that virtually all of the HF will remain undissociated, so the amount of F^- in the solution from HF dissociation will be negligible. Thus, the [HF] is about 1 M and the [F^-] is close to 0. This will be especially true once we have added more F^-, the addition of which will even further suppress the dissociation of HF.

We want the ratio of Base/Acid to be 0.66, so we will need [Base]/1M = 0.66. Thus, [F^-] should be about 0.66 M. For 100 mL of solution, then, we will want to add 0.066 moles (0.1 L x 0.66 M) of F^-. Since we are adding NaF as our source of F^-, and since NaF completely dissociates in water, we need 0.066 moles of NaF. Thus, 0.066 moles x 41.99 g/mol = 2.767 g.

Note that, since the conjugate acid and the conjugate base are both mixed into the same volume of solution in the buffer, the ratio of "Base/Acid" is the same whether we use a ratio of the "concentration of base over concentration of acid," OR a ratio of "moles of base over moles of acid." The pH of the solution does not, it turns out, depend on the volume! (This is only true so long as the solution does not get so dilute that the autoionization of water becomes an important source of H^+ or OH^-. Such dilute solutions are rarely used as buffers, however.)

References

1. Brown, et al. Chemistry:The Central Science. 11th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2008.
2. Chang, Raymond. General Chemistry:The Essential Concepts. 3rd ed. New York: Mcgraw Hill, 2003
3. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

Outside Links

- Urbansky, Edward T.; Schock, Michael R. "Understanding, Deriving, and Computing Buffer Capacity." *J. Chem. Educ.* **2000** *1640.*.

Contributors

- Jose Pietri (UCD), Donald Land (UCD)

8.10: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an electron-pair transfer reaction, clearly identifying the donor and acceptor.
- Give an example of a *Lewis acid-base reaction* that does not involve protons.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

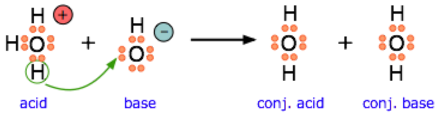
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

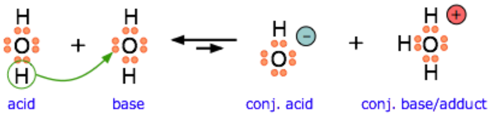
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



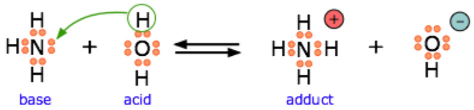
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

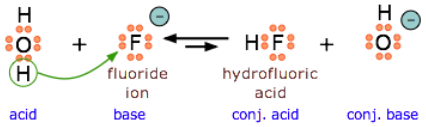
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



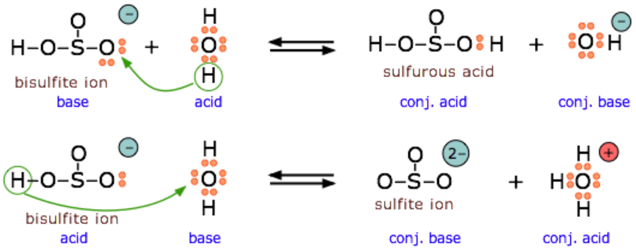
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$BF_3 + NH_3 \rightarrow F_3B{-}NH_3 \tag{8.10.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

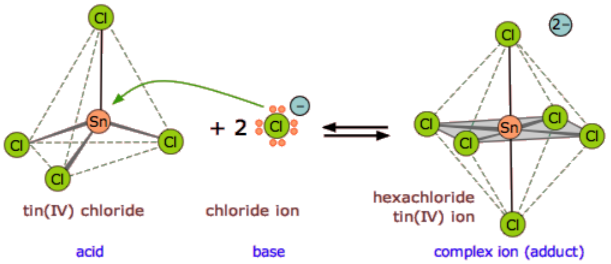


Figure 8.10.1: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

? Exercise 8.10.1

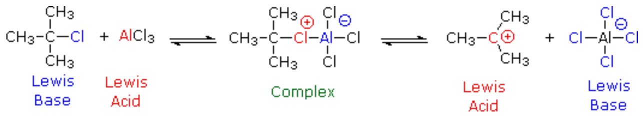
Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4{}^-$

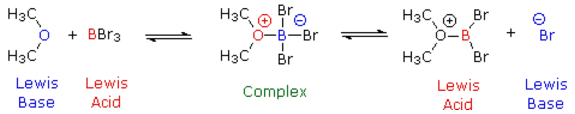
b. $\mathrm{SnS_2 + S^{2-} \rightarrow SnS_3^{2-}}$
c. $\mathrm{Cd(CN)_2 + 2\,CN{-} \rightarrow Cd(CN)_4^{2+}}$
d. $\mathrm{AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^{+} + Cl{-}}$
e. $\mathrm{Fe^{2+} + NO \rightarrow Fe(NO)^{2+}}$
f. $\mathrm{Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:

1



2



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $\mathrm{AlCl_3}$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table 8.10.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 8.10.1 indicates:

Table 8.10.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\,CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\,C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\,HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\,HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\,H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

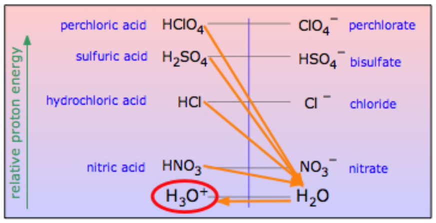


Figure 8.10.2: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

8.11: Acid/Base (Exercises)

CHAPTER OVERVIEW

9: Electrochemistry

9.1: Oxidation-Reduction Reactions

Skills to Develop

- To identify oxidation–reduction reactions in solution.

The term oxidation was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When exposed to air, aluminum metal develops a continuous, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions (O^{2-}). Because the metals have lost electrons to oxygen, they have been oxidized; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been reduced, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction. Therefore, these reactions are known as oxidation-reduction reactions, or "redox" reactions for short.

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

Originally, the term reduction referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water vapor). The reaction is as follows:

$$\mathrm{Cu_2O(s) + H_2(g) \rightarrow 2\,Cu(s) + H_2O(g)} \tag{9.1.1}$$

Oxidation-reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants by a transfer of electrons, which follows the mnemonic "oxidation is loss, reduction is gain", or **"oil rig"**. The **oxidation state** of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as O_2 or H_2, are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is

$$\mathrm{4\,Al(s) + 3\,O_2 \rightarrow 2\,Al_2O_3(s)} \tag{9.1.2}$$

Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of −2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of +3 in the product, so aluminum has been oxidized. In the formation of Al_2O_3, electrons are transferred as follows (the small overset number emphasizes the oxidation state of the elements):

$$4\overset{0}{\mathrm{Al}} + 3\overset{0}{\mathrm{O}}_2 \rightarrow \mathrm{4\,Al^{3+} + 6\,O^{2-}} \tag{9.1.3}$$

Equation 9.1.1 and Equation 9.1.2 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must equal the total of electrons gained to preserve electrical neutrality. In Equation 9.1.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned}
\text{electrons lost} &= 4\text{ Al atoms} \times \frac{3\,e^- \text{ lost}}{\text{Al atom}} \\
&= 12\,e^- \text{ lost} \\
\text{electrons gained} &= 6\text{ O atoms} \times \frac{2\,e^- \text{ gained}}{\text{O atom}} \\
&= 12\,e^- \text{ gained}
\end{aligned}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained. An additional example of a redox reaction, the reaction of sodium metal with chlorine is illustrated in Figure 9.1.1.

> *In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.*

Assigning Oxidation Numbers

Assigning oxidation numbers to the elements in binary ionic compounds is straightforward: the oxidation numbers of the elements are identical to the charges on the monatomic ions. Previously, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 9.1.1), magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. However, we can still assign oxidation states to the elements involved by treating them as if they were ionic (that is, as if all the bonding electrons were transferred to the more attractive element). Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

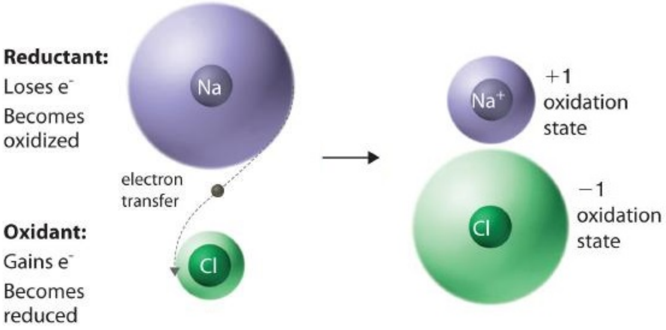


***Figure 9.1.1**: The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom. The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.*

A set of rules for assigning oxidation numbers to atoms in chemical compounds follows.

Rules for Assigning Oxidation Numbers

1. The oxidation number of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation number of a monatomic ion is the same as its charge—for example, $Na^+ = +1$, $Cl^- = -1$.
3. The oxidation number of fluorine in chemical compounds is always −1. Other halogens usually have oxidation states of −1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation number of +1 in its compounds with nonmetals and −1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation number of −2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the oxidation number of oxygen is determined by the oxidation number of the other elements present.
6. The sum of the oxidation numbers of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

> *Nonintegral (fractional) oxidation numbers are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states.*

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl, for example, Na has an oxidation state of +1 and Cl is −1. The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you will discover in Chapter 6. Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in OF_2 but −½ in KO_2. Note that an oxidation state of −½ for O in KO_2 is perfectly acceptable.

The reduction of copper(I) oxide shown in Equation 9.1.4 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of

+1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of −2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: 2(+1) + (−2) = 0. So the oxidation states are as follows:

$$\overset{+1}{\mathrm{Cu}}_2\overset{-2}{\mathrm{O}}(s) + \overset{0}{\mathrm{H}}_2(g) \rightarrow 2\overset{0}{\mathrm{Cu}}(s) + \overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}(g) \tag{9.1.4}$$

Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen (0 → +1) to copper (+1 → 0). Thus, this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

$$\text{electrons lost} = 2\; H\,\text{atoms} \times \frac{1\; e^-\ \text{lost}}{H\,\text{atom}} = 2\; e^-\ \text{lost} \tag{9.1.5}$$

$$\text{electrons gained} = 2\; Cu\,\text{atoms} \times \frac{1\; e^-\ \text{gained}}{Cu\,\text{atom}} = 2\; e^-\ \text{gained} \tag{9.1.6}$$

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation–reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

Example 9.1.1: Oxidation States

Assign oxidation states to all atoms in each compound.

a. sulfur hexafluoride (SF_6)
b. methanol (CH_3OH)
c. ammonium sulfate [(NH_4)2SO_4]
d. magnetite (Fe_3O_4)
e. ethanoic (acetic) acid (CH_3CO_2H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

Solution:

a. We know from rule 3 that fluorine always has an oxidation state of −1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of −6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF_6), the oxidation state of sulfur must be +6:

[(6 F atoms)(−1)] + [(1 S atom) (+6)] = 0

b. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and −2, respectively. Because methanol has no net charge, carbon must have an oxidation state of −2:

[(4 H atoms)(+1)] + [(1 O atom)(−2)] + [(1 C atom)(−2)] = 0

c. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 2.4 "Common Polyatomic Ions and Their Names"). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of −3:

[(4 H atoms)(+1)] + [(1 N atom)(−3)] = +1, the charge on the NH_4^+ ion

For SO42−, oxygen has an oxidation state of −2 (rule 5), so sulfur must have an oxidation state of +6:

[(4 O atoms) (−2)] + [(1 S atom)(+6)] = −2, the charge on the sulfate ion

d. Oxygen has an oxidation state of −2 (rule 5), giving an overall charge of −8 per formula unit. This must be balanced by the positive charge on three iron atoms, giving an oxidation state of +8/3 for iron:

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

Fractional oxidation states are allowed because oxidation states are a somewhat arbitrary way of keeping track of electrons. In fact, Fe_3O_4 can be viewed as having two Fe^{3+} ions and one Fe^{2+} ion per formula unit, giving a net positive charge of +8 per formula unit. Fe_3O_4 is a magnetic iron ore commonly called magnetite. In ancient times, magnetite was known as lodestone because it could be used to make primitive compasses that pointed toward Polaris (the North Star), which was called the "lodestar."

e. Initially, we assign oxidation states to the components of CH_3CO_2H in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and −2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of

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

So the oxidation state of carbon must also be zero (rule 6). This is, however, an average oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($-CH_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of −3. Similarly, the carbon atom of the carboxylic acid group ($-CO_2H$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of −2 and +1 to the oxygen and hydrogen atoms, respectively, leading to a net charge of

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

To obtain an electrically neutral carboxylic acid group, the charge on this carbon must be +3. The oxidation states of the individual atoms in acetic acid are thus

$$\underset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\underset{-2}{O_2}\overset{+1}{H} \tag{9.1.7}$$

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

Exercise 9.1.1: Oxidation States

Assign oxidation states to all atoms in each compound.

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

Answer a

Ba, +2; F, −1

Answer b

C, 0; H, +1; O, −2

Answer c

K, +1; Cr, +6; O, −2

Answer d

Cs, +1; O, −½

Answer e

C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

Types of Redox Reactions

Many types of chemical reactions are classified as redox reactions, and it would be impossible to memorize all of them. However, there are a few important types of redox reactions that you are likely to encounter and should be familiar with. These include:

- **Synthesis** reactions: The formation of any compound directly from the elements is a redox reaction, for example, the formation of water from hydrogen and oxygen:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \tag{9.1.8}$$

- **Decomposition** reactions: Conversely, the decomposition of a compound to its elements is also a redox reaction, as in the electrolysis of water:

$$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \tag{9.1.9}$$

- **Combustion** reactions: Many chemicals combust (burn) with oxygen. In particular, organic chemicals such as hydrocarbons burn in the presence of oxygen to produce carbon dioxide and water as the products:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \tag{9.1.10}$$

The following sections describe another important class of redox reactions: single-displacement reactions of metals in solution.

Redox Reactions of Solid Metals in Aqueous Solution

A widely encountered class of oxidation–reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure $9.1.2$). Rust is formed from a complex oxidation–reduction reaction involving dilute acid solutions that contain Cl^- ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with HCl(aq) to produce iron(II) chloride and hydrogen gas:

$$Fe(s) + 2\,HCl(aq) \rightarrow FeCl_2(aq) + H_2(g) \tag{9.1.11}$$

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

Figure $9.1.2$: *Rust Formation. The corrosion process involves an oxidation–reduction reaction in which metallic iron is converted to $Fe(OH)_3$, a reddish-brown solid.*

Many metals dissolve through reactions of this type, which have the general form

$$\text{metal} + \text{acid} \rightarrow \text{salt} + \text{hydrogen} \tag{9.1.12}$$

Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids. In the presence of these acids, lead dissolves:

$$Pb(s) + 2\,H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g) \tag{9.1.13}$$

Consequently, it has been speculated that both the water and the food consumed by Romans contained toxic levels of lead, which resulted in widespread lead poisoning and eventual madness. Perhaps this explains why the Roman Emperor Caligula appointed his favorite horse as consul!

Single-Displacement Reactions

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 9.1.14) and the reduction of silver salts by copper (Equation 9.1.15 and Figure 9.1.3):

$$\mathrm{Zn(s)+Fe^{2\,+}(aq)\rightarrow Zn^{2\,+}(aq)+Fe(s)} \tag{9.1.14}$$

$$\mathrm{Cu(s)+2\,Ag^{+}(aq)\rightarrow Cu^{2\,+}(aq)+2\,Ag(s)} \tag{9.1.15}$$

The reaction in Equation 9.1.14 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.

***Figure 9.1.3**: The Single-Displacement Reaction of Metallic Copper with a Solution of Silver Nitrate. When a copper coil is placed in a solution of silver nitrate, silver ions are reduced to metallic silver on the copper surface, and some of the copper metal dissolves. Note the formation of a metallic silver precipitate on the copper coil and a blue color in the surrounding solution due to the presence of aqueous $\mathrm{Cu^{2\,+}}$ ions. Figure used with permission (CC BY-SA 3.0; Toby Hudson).*

The Activity Series

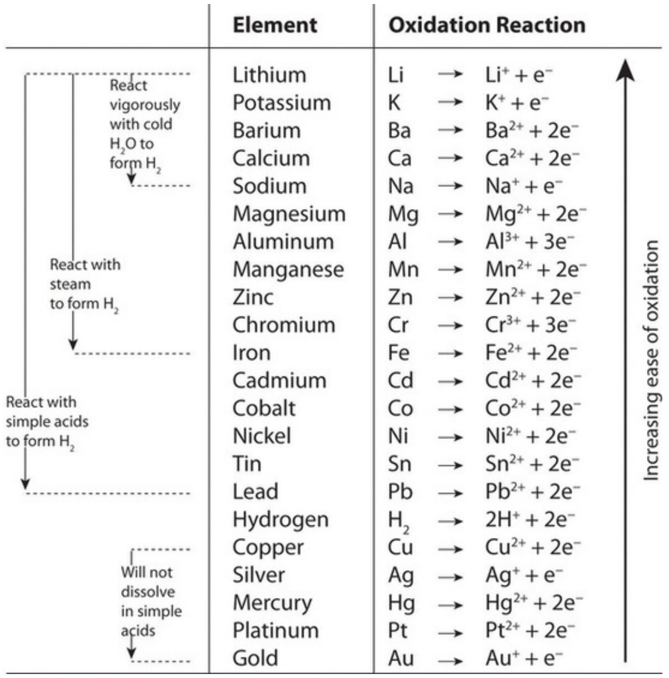
By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing $\mathrm{Zn_2^+}$. Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:

$$\mathrm{Zn(s)+Mg^{2\,+}(aq)\not\rightarrow Zn^{2\,+}(aq)+Mg(s)} \tag{9.1.16}$$

$$\mathrm{Mg(s)+Zn^{2\,+}(aq)\rightarrow Mg^{2\,+}(aq)+Zn(s)} \tag{9.1.17}$$

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

Pairwise reactions of this sort are the basis of the activity series (Figure 9.1.4), which lists metals and hydrogen in order of their relative tendency to be oxidized. The metals at the top of the series, which have the greatest tendency to lose electrons, are the alkali metals (group 1), the alkaline earth metals (group 2), and Al (group 13). In contrast, the metals at the bottom of the series, which have the lowest tendency to be oxidized, are the precious metals or coinage metals—platinum, gold, silver, and copper, and mercury, which are located in the lower right portion of the metals in the periodic table. You should be generally familiar with which kinds of metals are active metals, which have the greatest tendency to be oxidized. (located at the top of the series) and which are inert metals, which have the least tendency to be oxidized. (at the bottom of the series).



Element	Oxidation Reaction
Lithium	$Li \rightarrow Li^+ + e^-$
Potassium	$K \rightarrow K^+ + e^-$
Barium	$Ba \rightarrow Ba^{2+} + 2e^-$
Calcium	$Ca \rightarrow Ca^{2+} + 2e^-$
Sodium	$Na \rightarrow Na^+ + e^-$
Magnesium	$Mg \rightarrow Mg^{2+} + 2e^-$
Aluminum	$Al \rightarrow Al^{3+} + 3e^-$
Manganese	$Mn \rightarrow Mn^{2+} + 2e^-$
Zinc	$Zn \rightarrow Zn^{2+} + 2e^-$
Chromium	$Cr \rightarrow Cr^{3+} + 3e^-$
Iron	$Fe \rightarrow Fe^{2+} + 2e^-$
Cadmium	$Cd \rightarrow Cd^{2+} + 2e^-$
Cobalt	$Co \rightarrow Co^{2+} + 2e^-$
Nickel	$Ni \rightarrow Ni^{2+} + 2e^-$
Tin	$Sn \rightarrow Sn^{2+} + 2e^-$
Lead	$Pb \rightarrow Pb^{2+} + 2e^-$
Hydrogen	$H_2 \rightarrow 2H^+ + 2e^-$
Copper	$Cu \rightarrow Cu^{2+} + 2e^-$
Silver	$Ag \rightarrow Ag^+ + e^-$
Mercury	$Hg \rightarrow Hg^{2+} + 2e^-$
Platinum	$Pt \rightarrow Pt^{2+} + 2e^-$
Gold	$Au \rightarrow Au^+ + e^-$

Figure* 9.1.4*: The Activity Series

When using the activity series to predict the outcome of a reaction, keep in mind that *any element will reduce compounds of the elements below it in the series*. Because magnesium is above zinc in Figure 9.1.4, magnesium metal will reduce zinc salts but not vice versa. Similarly, the precious metals are at the bottom of the activity series, so virtually any other metal will reduce precious metal salts to the pure precious metals. Hydrogen is included in the series, and the tendency of a metal to react with an acid is indicated by its position relative to hydrogen in the activity series. *Only those metals that lie above hydrogen in the activity series dissolve in acids to produce* H_2. Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore do not corrode readily. Example 9.1.2 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions.

Example 9.1.2: Activity

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

a. A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
b. A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
c. Some sulfuric acid from a car battery is accidentally spilled on the lead cable terminals.

Given: reactants

Asked for: overall reaction and net ionic equation

Strategy:

A. Locate the reactants in the activity series in Figure 9.1.4 and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.
B. Write the net ionic equation for the redox reaction.

Solution:

1. **A** Aluminum is an active metal that lies above silver in the activity series, so we expect a reaction to occur. According to their relative positions, aluminum will be oxidized and dissolve, and silver ions will be reduced to silver metal. **B** The net ionic equation is as follows:

$$\mathrm{Al(s) + 3\,Ag^+(aq) \rightarrow Al^{3+}(aq) + 3\,Ag(s)}$$

   Recall from our discussion of solubilities that most nitrate salts are soluble. In this case, the nitrate ions are spectator ions and are not involved in the reaction.

2. **A** Mercury lies below lead in the activity series, so no reaction will occur.
3. **A** Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form H_2. **B** From our discussion of solubilities, recall that Pb^{2+} and SO_4^{2-} form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:

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

Lead(II) sulfate is the white solid that forms on corroded battery terminals.

Corroded battery terminals. *The white solid is lead(II) sulfate, formed from the reaction of solid lead with a solution of sulfuric acid.*

Exercise 9.1.2

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

a. A strip of chromium metal is placed in an aqueous solution of aluminum chloride.
b. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
c. A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

Answer a

$no\,reaction$

Answer b

$3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$

Answer c

$2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^-(aq) + 3H_2(g)$

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the **oxidation state method** (Table 9.1.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. There are many types of redox reactions. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 9.1.4), which arranges metals and H_2 in decreasing order of their tendency to be oxidized. Any metal will reduce metal ions below it in the activity series. **Active metals** lie at the top of the activity series, whereas **inert metals** are at the bottom of the activity series.

9.2: Standard Reduction Potentials

Skills to Develop

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

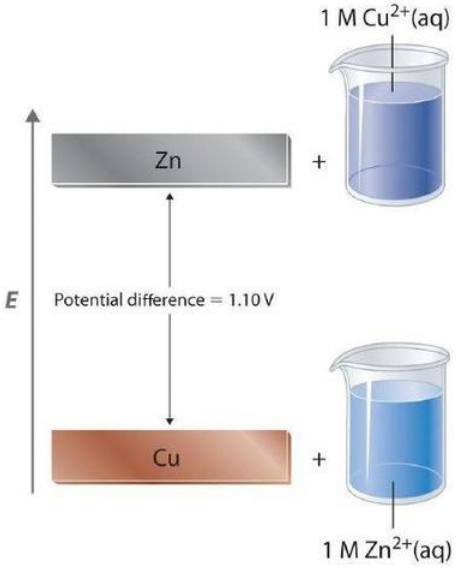


Figure $9.2.1$: *Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous \(Zn^{2+}\) ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the $Zn(s) + Cu^{2+}(aq)$ system is higher in energy by 1.10 V than the $Cu(s) + Zn^{2+}(aq)$ system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.*

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure $9.2.1$ but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**). Recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E^\circ = 0.59\ V \tag{9.2.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} \tag{9.2.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 9.2.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

> The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:
>
> $$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} \tag{9.2.3}$$

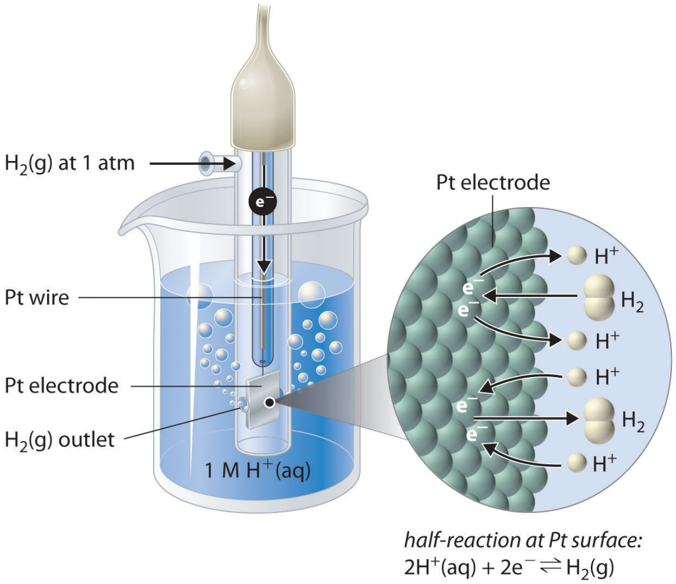


***Figure 9.2.2:** The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.*

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+.

The [H$^+$] in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 9.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{9.2.4}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

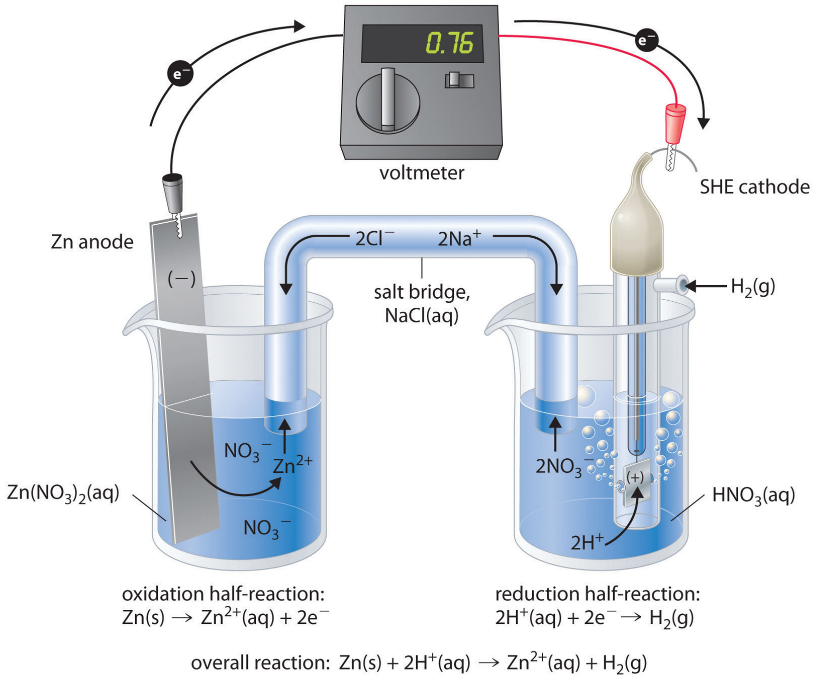


Figure 9.2.3: *Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is E°_{cell} = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form Zn^{2+}(aq) ions while H$^+$(aq) ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.*

Figure 9.2.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H$^+$ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{9.2.5}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ{}_{cathode} = 0V \tag{9.2.6}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E^\circ{}_{anode} = -0.76\ V \tag{9.2.7}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{9.2.8}$$

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} = 0.76\ V \tag{9.2.9}$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction.In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E^{\circ}{}_{cell} : 0\,V - (-0.76\,V) = 0.76\,V \tag{9.2.10}$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 9.2.3 but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E^{\circ}{}_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E^{\circ}{}_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{9.2.11}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E^{\circ}{}_{cathode} = 0.34\ V \tag{9.2.12}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E^{\circ}{}_{anode} = 0\ V \tag{9.2.13}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{9.2.14}$$

$$E^{\circ}{}_{cell} = E^{\circ}{}_{cathode} - E^{\circ}{}_{anode} = 0.34\ V \tag{9.2.15}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{9.2.16}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E^{\circ}{}_{cell}$:

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^{\circ}{}_{cathode} = 0.34\ V \tag{9.2.17}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E^{\circ}{}_{anode} = -0.76\ V \tag{9.2.18}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{9.2.19}$$

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} = 1.10\ V \tag{9.2.20}$$

This is the same value that is observed experimentally. If the value of $E^\circ{}_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E^\circ{}_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example $9.2.2$ and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E^\circ{}_{cell}$ means that the reaction will occur spontaneously as written. A negative $E^\circ{}_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

Example 9.2.1

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

anode: $Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.
B. Use Equation 9.2.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = −0.55$ V.

B Using the value given for $E^\circ{}_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 9.2.2:

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode}$$

$$0.27\ V = E°_{cathode} - (-0.55\ V)$$
$$E°_{cathode} = -0.28\ V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus E° = −(−0.28 V) = 0.28 V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

Exercise 9.2.1

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2e^{-} \rightarrow Hg(l)$
- anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

Answer

0.85 V

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. $E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode}$ The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E^\circ{}_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E^\circ{}_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

9.3 Cell Potential, Gibbs Free Energy, and Equilibrium

Skills to Develop

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with Ni^{2+}(aq) to form Ni(s) and Co^{2+}(aq) occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that $[Ni^{2+}]$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \mathrm{J}}{1\ \mathrm{V}} = 1\ \mathrm{C} = \mathrm{A \cdot s} \tag{1}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{align} F &= (1.60218 \times 10^{-19}\ \mathrm{C})\left(\frac{6.02214 \times 10^{23}}{1\ \mathrm{mol\ e^-}}\right) \tag{2} \\ &= 9.64855 \times 10^{4}\ \mathrm{C/mol\ e^-} \simeq 96,486/(\mathrm{V \cdot mol\ e^-}) \tag{3} \end{align}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell} \tag{4}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell} \tag{5}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{6}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of $E°_{cell}$.

Example 1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG° for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E°, write the overall reaction and calculate $E°_{cell}$.
B. Determine the number of electrons transferred in the overall reaction. Then use Equation 6 to calculate ΔG°. If ΔG° is negative, then the reaction is spontaneous.

Solution:

A As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E°. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E° values:

$$\text{cathode:} \quad \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} \quad E^\circ_{\text{cathode}} = 1.23\ \mathrm{V} \tag{7}$$

$$\text{anode:} \quad \mathrm{2Br^-(aq) \rightarrow Br_2(aq) + 2e^-} \quad E^\circ_{\text{anode}} = 1.09\ \mathrm{V} \tag{8}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E° is not affected:

$$\text{cathode:} \quad \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} \quad E^\circ_{\text{cathode}} = 1.23\ \mathrm{V} \tag{9}$$

$$\text{anode:} \quad \mathrm{6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-} \quad E^\circ_{\text{anode}} = 1.09\ \mathrm{V} \tag{10}$$

$$\text{overall:} \quad \mathrm{Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)} \quad E^\circ_{\text{cell}} = 0.14\ \mathrm{V} \tag{11}$$

B We can now calculate ΔG° using Equation 6. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\Delta G^\circ = -(n)(F)(E^\circ_{\text{cell}}) = -(6\ \text{mole})[96,468\ \mathrm{J/(V \cdot mol)}(0.14\ \mathrm{V})] \tag{12}$$

$$= -8.1\ \times 10^4\ \mathrm{J} \tag{13}$$

$$= -81\ \mathrm{kJ/mol\ Cr_2O_7^{2-}} \tag{14}$$

Thus ΔG° is −81 kJ for the reaction as written, and the reaction is spontaneous.

Exercise 1

Use the data in Table P2 to calculate ΔG° for the reduction of ferric ion by iodide:

$$\mathrm{2\,Fe^{3\,+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2\,+}(aq) + I_2(s)}$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of Fe^{3+}(aq) to Fe(s) is not listed in the table, but two related reductions are given:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad E^\circ = +0.77V \tag{15}$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(aq) \quad E^\circ = -0.45V \tag{16}$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E° is not a state function. However, because ΔG° is a state function, the sum of the ΔG° values for the individual reactions gives us ΔG° for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E° for the overall half-reaction, we first must add the values of ΔG° (= −nFE°) for each individual half-reaction to obtain ΔG° for the overall half-reaction:

$$\mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)} \quad \Delta G^\circ = -(1)(F)(0.77\ \mathrm{V}) \tag{17}$$

$$\mathrm{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)} \quad \Delta G^\circ = -(2)(F)(-.045\ \mathrm{V}) \tag{18}$$

$$\mathrm{Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)} \quad \Delta G^\circ = [-(1)(F)(0.77\ \mathrm{V})] + [-(2)(F)(-0.45\ \mathrm{V})] \tag{19}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V) \tag{20}$$

Three electrons (n = 3) are transferred in the overall reaction, so substituting into Equation 6 and solving for E° gives the following:

$$\Delta G^\circ = -nFE^\circ_{\mathrm{cell}} \tag{21}$$

$$F(0.13\ \mathrm{V}) = -(3)(F)(E^\circ_{\mathrm{cell}}) \tag{22}$$

$$E^\circ = -\frac{0.13\ \mathrm{V}}{3} = -0.043\ \mathrm{V} \tag{23}$$

This value of E° is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E° for half-reactions cannot be added to give E° for the sum of the half-reactions; only values of ΔG° = −nFE°$_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K \tag{24}$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 6), we can write

$$-nFE^\circ_{cell} = -RT \ln K \tag{25}$$

Rearranging this equation,

$$E^\circ_{\mathrm{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{26}$$

For T = 298 K, Equation 25 can be simplified as follows:

$$E^\circ_{\mathrm{cell}} = \left(\frac{RT}{nF}\right) \ln K = \left[\frac{[8.314\ \mathrm{J/(mol \cdot K)}(298\ \mathrm{K})]}{n[96,486\ \mathrm{J/(V \cdot mol)}]}\right] 2.303 \log K = \left(\frac{0.0591\ \mathrm{V}}{n}\right) \log K \tag{27}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E°$_{cell}$.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 27 to solve for log K and then K.

Solution:

A The relevant half-reactions and potentials from Table P2 are as follows:

$$\text{cathode:} \quad \mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)} \qquad E^\circ_{\mathrm{cathode}} = 1.69\ \mathrm{V} \tag{28}$$

$$\text{anode:} \quad \mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-} \qquad E^\circ_{\mathrm{anode}} = -0.36\ \mathrm{V} \tag{29}$$

$$\text{overall:} \quad \mathrm{Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)} \qquad E^\circ_{\mathrm{cell}} = 2.05\ \mathrm{V} \tag{30}$$

B Two electrons are transferred in the overall reaction, so n = 2. Solving Equation 27 for log K and inserting the values of n and E°,

$$\log K = \frac{nE^\circ}{0.0591 \text{ V}} = \frac{2(2.05 \text{ V})}{0.0591 \text{ V}} = 69.37 \tag{31}$$

$$K = 2.3 \times 10^{69} \tag{32}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 3

Use the data in Table P2 to calculate the equilibrium constant for the reaction of Sn^{2+}(aq) with oxygen to produce Sn^{4+}(aq) and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightleftharpoons 2Sn^{4+}_{(aq)} + 2H_2O_{(l)} \tag{33}$$

Answer

1.2×10^{73}

Figure 1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity (ΔG° < 0). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.

Figure 1: *The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and* $E°_{cell}$*. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and* $E°_{cell}$ *and the magnitude of K determine the direction of spontaneous reaction under standard conditions.*

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro’s number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

9.4: Batteries: Using Chemistry to Generate Electricity

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure $9.4.1$). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

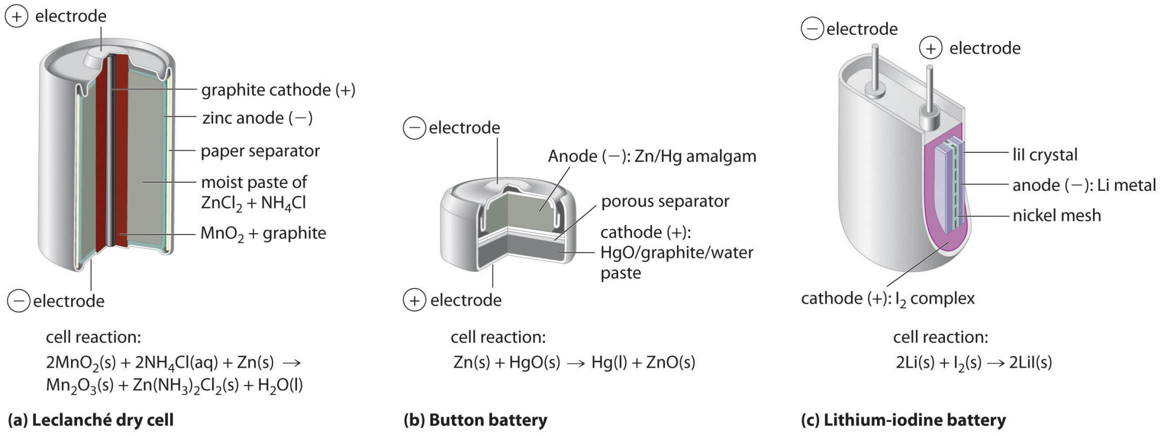


Figure $9.4.1$: *Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.*

The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure $9.4.1$). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2MnO_{2(s)} + 2NH^+_{4(aq)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} \tag{9.4.1}$$

- anode (oxidation):

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \tag{9.4.2}$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall:

$$2MnO_{2(s)} + 2NH_4Cl_{(aq)} + Zn_{(s)} \rightarrow Mn_2O_{3(s)} + Zn(NH_3)_2Cl_{2(s)} + H_2O_{(l)} \tag{9.4.3}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.

Source: Photo courtesy of Mitchclanky2008, http://www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)} \tag{9.4.4}$$

- anode (oxidation):

$$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^- \tag{9.4.5}$$

- overall:

$$Zn_{(s)} + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)} \tag{9.4.6}$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 (part (b) in Figure 9.4.1).

Button batteries. Photo courtesy of Gerhard H Wrodnigg, Images used with permission from Wikipedia

The cathode and overall reactions and cell output for these two types of button batteries are as follows:

- cathode (Hg):

$$HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)} \tag{9.4.7}$$

- overall (Hg):

$$Zn_{(s)} + 2HgO_{(s)} \rightarrow Hg_{(l)} + ZnO_{(s)} \tag{9.4.8}$$

with $E_{cell} = 1.35\,V$

- cathode (Ag):

$$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)} \tag{9.4.9}$$

- overall (Ag):

$$Zn_{(s)} + 2Ag_2O_{(s)} \rightarrow 2Ag_{(s)} + ZnO_{(s)} \tag{9.4.10}$$

with $E_{cell} = 1.6\,V$

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually “dry.” They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{9.4.11}$$

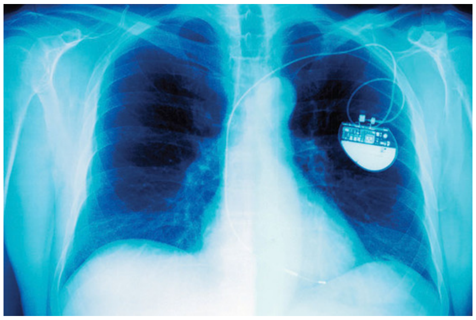
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{9.4.12}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{9.4.13}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: *An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.*

As shown in part (c) in Figure $9.4.1$, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure $9.4.2$, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

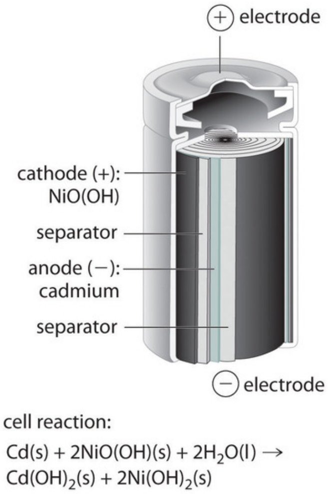


Figure 9.4.2: *The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.*

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{9.4.14}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{9.4.15}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{9.4.16}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

$$NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \tag{9.4.17}$$

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

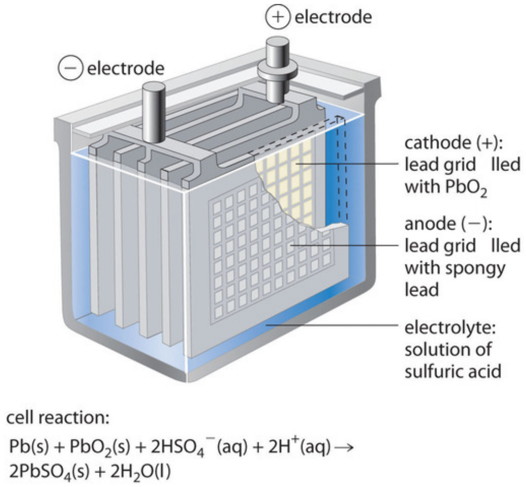


***Figure 9.4.3**: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.*

As shown in Figure 9.4.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

$$PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \tag{9.4.18}$$

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{9.4.19}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{9.4.20}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.

A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (https://www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{9.4.21}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

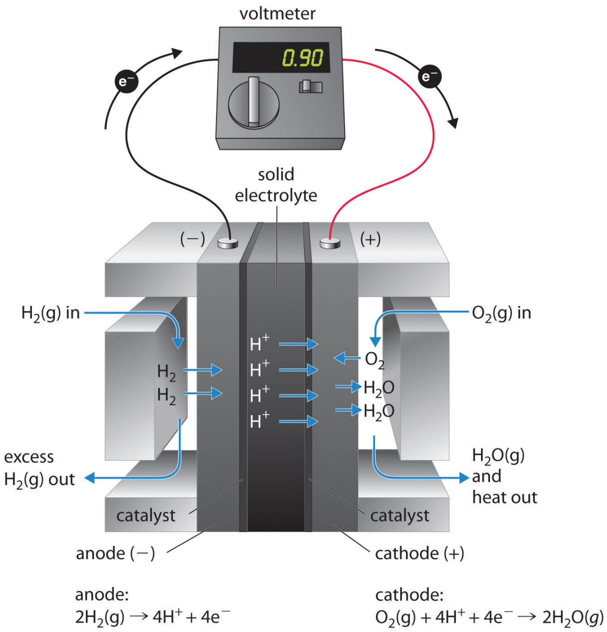


Figure 9.4.4: *A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.*

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of H_2(g) and O_2(g), as illustrated in Figure 9.4.4. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{9.4.22}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{9.4.23}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{9.4.24}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

9.5 Driving Reactant-Favored Reactions Using Electricity

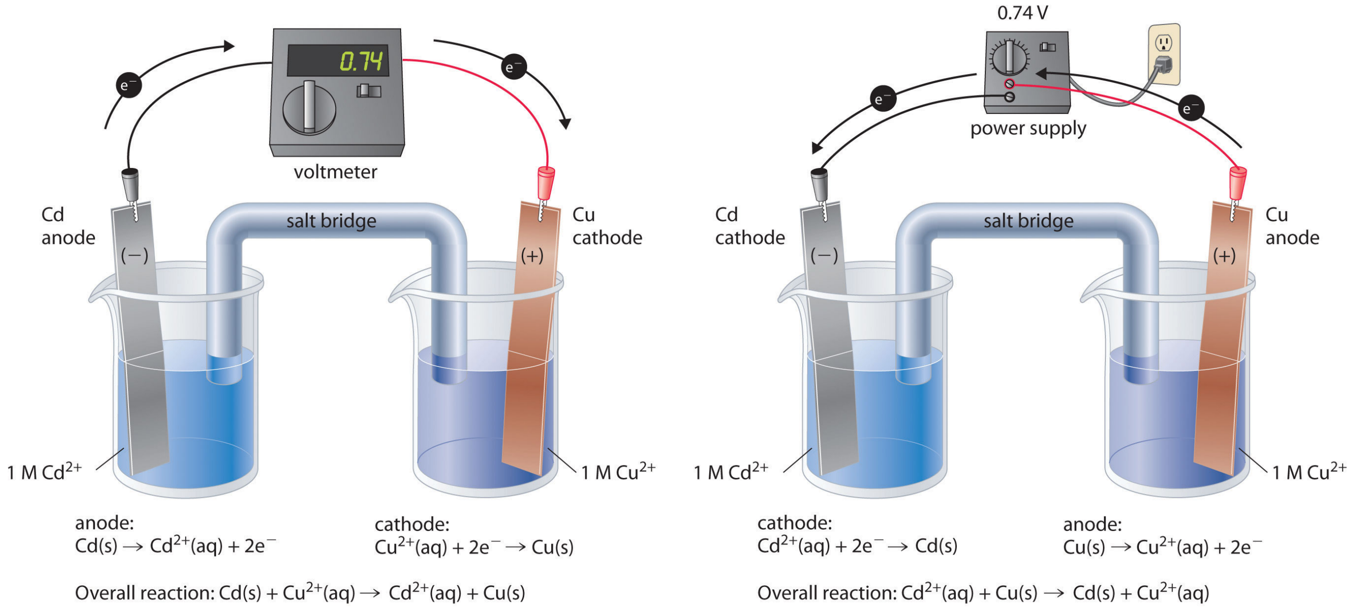
Skills to Develop

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure $1a$).



(a) Galvanic cell

(b) Electrolytic cell

Figure 1: *An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it.*

The overall reaction is as follows:

$$\mathrm{Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)} \tag{1}$$

with $E^\circ{}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G° < 0$):

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \tag{2}$$

$$= -(2\ \text{mol e}^-)[96,486\ \text{J/(V}\cdot\text{mol)}](0.74\ \text{V}) \tag{3}$$

$$= -140\ \text{kJ (per mole Cd)} \tag{4}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure 1b). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- cathode:

$$\mathrm{Cd^{2\,+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{5}$$

with $E^\circ_{cathode} = -0.40\,V$

- anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2\,+}(aq) + 2\,e^-} \tag{6}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall:

$$\mathrm{Cd^{2\,+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2\,+}(aq)} \tag{7}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 1.

***Table* 1**: *Comparison of Galvanic and Electrolytic Cells*

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten $NaCl$, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{8}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of $NaCl$ (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten $NaCl$ in a Downs cell (Figure 2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the $NaCl$ to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

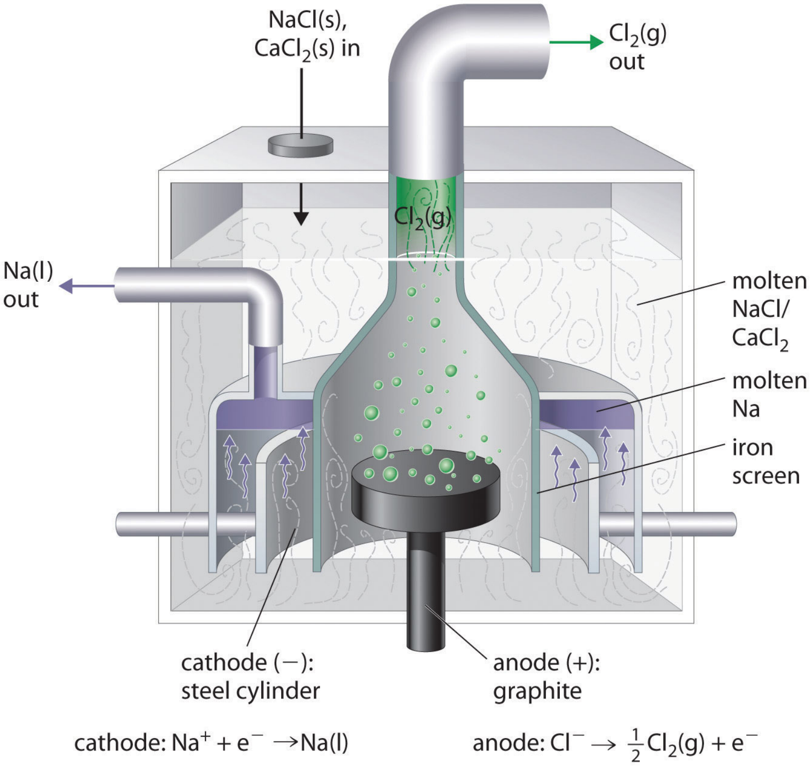


Figure 2: *A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.*

Similarly, in the Hall–Herout process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2Al_2O_{3(l)} + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)} \tag{9}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Herout process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Herout process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 3).

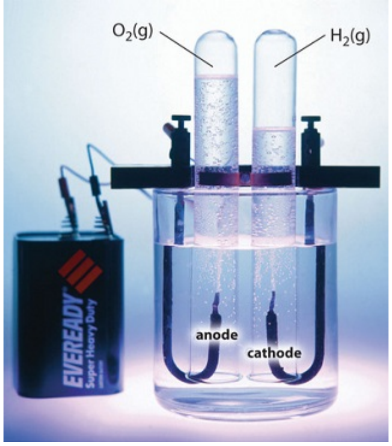


Figure 3: *The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode.*

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{10}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{11}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{12}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{13}$$

$$E_{\text{cell}} = -1.23\text{ V} - \left(\frac{0.0591\text{ V}}{4}\right)\log(1) = -1.23\text{ V} \tag{14}$$

Thus E_{cell} is −1.23 V, which is the value of E°_{cell} if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 4.

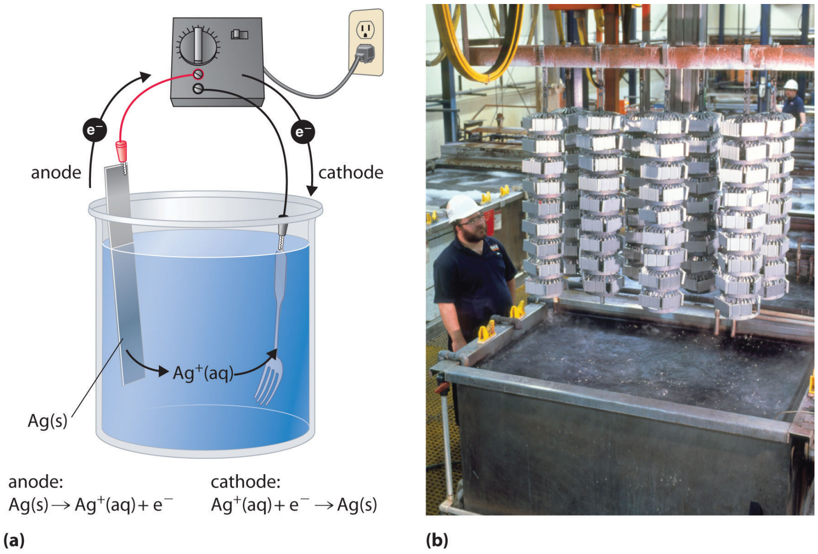


Figure 3: *Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag+ solution and applying the correct potential.*

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$Ag^+_{(aq)} + e- \rightarrow Ag_{(s)} \qquad E^\circ{}_{cathode} = 0.80V \tag{15}$$

- anode (silver bar):

$$Ag_{(s)} \rightarrow Ag^+_{(aq)} \qquad E^\circ{}_{anode} = 0.80V \tag{16}$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell}$ = 0 V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$C = A \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

9.6 Undesirable Redox Reactions

Skills to Develop

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth’s moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3 \cdot xH_2O$), commonly known as rust, that does not provide a tight protective film (Figure 1). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

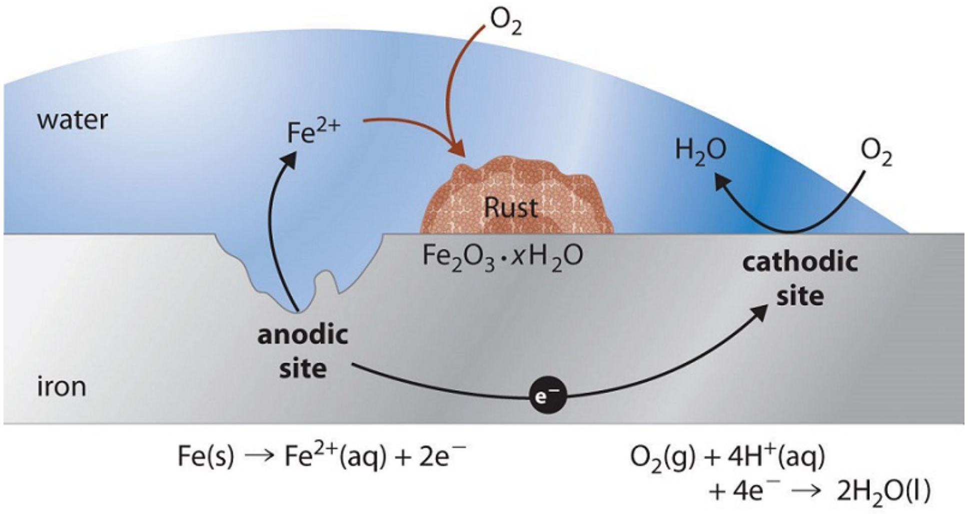


***Figure 1**: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \cdot xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.*

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \quad E^\circ = 1.23\ V \tag{1}$$

- at anode:

$$Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad E^\circ = -0.45\ V \tag{2}$$

- overall:

$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad E^\circ = 1.68\ V \tag{3}$$

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + (2+4x)H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+_{(aq)} \tag{4}$$

The sign and magnitude of E° for the corrosion process (Equation 3) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 2).

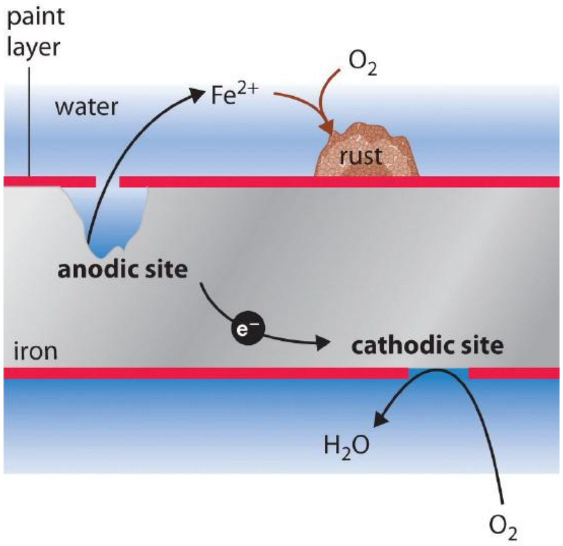


Figure 2: *Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to* Fe^{2+}*(aq) at the less exposed site (the anode). Rust is formed when* Fe^{2+}*(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.*

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings.

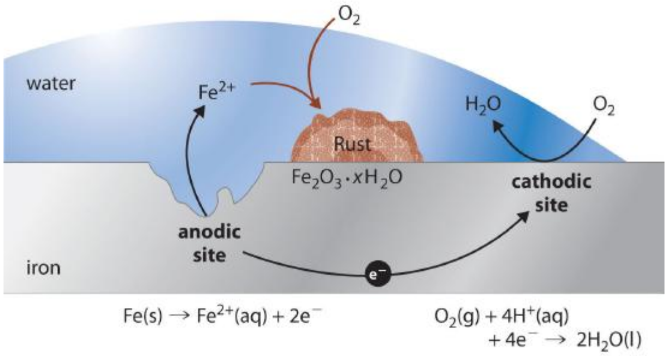


***Figure 3**: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.*

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} (E° = −0.14 V) and Fe^{2+} (E° = −0.45 V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn (E° = −0.76 V for $Zn^{2+} + 2e^- \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{5}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{6}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{7}$$

The more reactive metal reacts with oxygen and will eventually dissolve, "sacrificing" itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.

Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

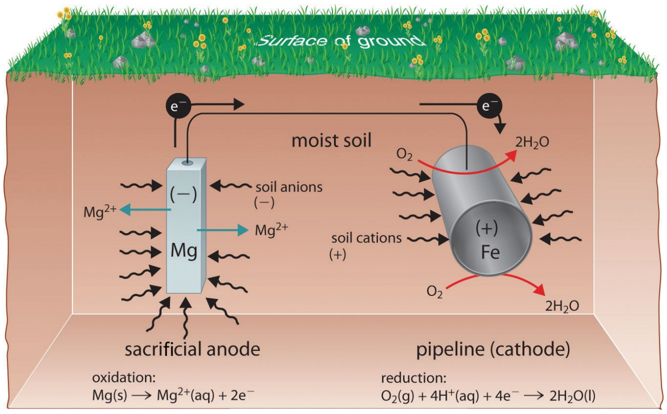


***Figure 4**: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.*

Example 1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution:

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of E° than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\text{cathode:} \quad \mathrm{O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)} \qquad E^\circ_{\text{cathode}} = 1.23\text{ V} \tag{8}$$

$$\text{anode:} \quad \mathrm{Fe(s) \rightarrow Fe^{2+} + 2e^-} \qquad E^\circ_{\text{anode}} = -0.45\text{ V} \tag{9}$$

$$\text{overall:} \quad \mathrm{2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)} \qquad E^\circ_{\text{overall}} = 1.68\text{ V} \tag{10}$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 7).

Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

Exercise 1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

Answer a

Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

Index

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: CHM 120 - Survey of General Chemistry(Neils)

Webpages: 105

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC-SA 4.0: 86.7% (91 pages)
- Undeclared: 7.6% (8 pages)
- CC BY 4.0: 3.8% (4 pages)
- Public Domain: 1% (1 page)
- CC BY-SA 4.0: 1% (1 page)

By Page

- CHM 120 - Survey of General Chemistry(Neils) - *CC BY-NC-SA 4.0*
  - Front Matter - *CC BY-NC-SA 4.0*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Matter and Energy - *CC BY-NC-SA 4.0*
    - 1.1 The Terms of Science - *CC BY-NC-SA 4.0*
    - 1.2: A First Look at the Periodic Table - *CC BY-NC-SA 4.0*
    - 1.3: The Classification of Matter - *CC BY-NC-SA 4.0*
    - 1.4: A First Look at Energy - *CC BY-NC-SA 4.0*
    - 1.5: Making Measurements - *CC BY 4.0*
    - 1.6: Limits on Measurements - *CC BY 4.0*
    - 1.7: Dimensional Analysis - *CC BY 4.0*
    - 1.8: Matter, Measurement, and Problem Solving (Exercises) - *CC BY-NC-SA 4.0*
  - 2: Atomic Structure - *CC BY-NC-SA 4.0*
    - 2.1: Modern Atomic Theory and the Laws That Led to It - *CC BY-NC-SA 4.0*
    - 2.2 The Structure of the Atom - *CC BY 4.0*
    - 2.3 Molar Mass - Counting Atoms by Weighing Them - *CC BY-NC-SA 4.0*
    - 2.4 Nuclear Reactions - *CC BY-NC-SA 4.0*
    - 2.5 The Belt of Stability - Predicting the Type of Radioactivity - *CC BY-NC-SA 4.0*
    - 2.6 Half-lives and the Rate of Radioactive Decay - *CC BY-NC-SA 4.0*
    - 2.7 Mass Defect - The Source of Nuclear Energy - *CC BY-NC-SA 4.0*
    - 2.8 Nuclear Energy - Fission and Fusion - *CC BY-NC-SA 4.0*
    - 2.9 The Nature of Light - *CC BY-NC-SA 4.0*
    - 2.10 Quantum Mechanics and The Atom - *CC BY-NC-SA 4.0*
    - 2.11 Trends of the Periodic Table - *CC BY-NC-SA 4.0*
    - 2.12 Example Problems - *CC BY-NC-SA 4.0*
  - 3: Chemical Formulas and Bonding - *CC BY-NC-SA 4.0*
    - 3.1 An Atomic-Level Perspective of Ionic and Covalent Compounds - *CC BY-NC-SA 4.0*
    - 3.2 Composition of Compounds - *CC BY-NC-SA 4.0*
    - 3.3 Chemical Bonds - *CC BY-NC-SA 4.0*
    - 3.4 Ionic Compounds: Formulas and Names - *CC BY-NC-SA 4.0*
    - 3.5 Covalently-Bonded Species: Formulas and Names - *CC BY-NC-SA 4.0*
    - 3.6 Electronegativity and Bond Polarity - *CC BY-NC-SA 4.0*
    - 3.7 Lewis Structures - *CC BY-NC-SA 4.0*
    - 3.8 Resonance and Formal Charge Revisited - *CC BY-NC-SA 4.0*
    - 3.9 Exceptions to the Octet Rule - *CC BY-NC-SA 4.0*
    - 3.10 Shapes of Molecules - VSEPR Theory and Valence Bond Theory - *CC BY-NC-SA 4.0*
    - 3.11 Practice Problems - *CC BY-NC-SA 4.0*
  - 4: Intermolecular Forces, Phases, and Solutions - *CC BY-NC-SA 4.0*
    - 4.1 Water in Zero Gravity - an Introduction to Intermolecular Forces - *Public Domain*
    - 4.2 Intermolecular Forces - *CC BY-NC-SA 4.0*
    - 4.3 Application of IMFs: Evaporation, Vapor Pressure, and Boiling Points - *CC BY-NC-SA 4.0*
    - 4.4: Intermolecular Forces in Action: Surface Tension, Viscosity, and Capillary Action - *CC BY-NC-SA 4.0*
    - 4.5: Solids, Liquids, and Gases: A Molecular Comparison - *CC BY-NC-SA 4.0*
    - 4.6 Phase Changes - *CC BY-NC-SA 4.0*

    - 4.7: Pressure: The Result of Particle Collisions - *CC BY-NC-SA 4.0*
    - 4.8: Gases - *CC BY-NC-SA 4.0*
    - 4.9 Solutions - What Mixes Together and Why - *CC BY-SA 4.0*
    - 4.10 Factors Affecting Solubility - *CC BY-NC-SA 4.0*
    - 4.11 Suspensions and Colloids - *CC BY-NC-SA 4.0*
    - 4.12 Practice Problems - *CC BY-NC-SA 4.0*
    - Intermolecular Forces - *CC BY-NC-SA 4.0*
- 5: The Numbers Game - Solutions and Stoichiometry - *CC BY-NC-SA 4.0*
    - 5.1 Expressing Solution Concentration - *CC BY-NC-SA 4.0*
    - 5.2 Types of Aqueous Solutions and Solubility - *CC BY-NC-SA 4.0*
    - 5.3 Colligative Properties and Freezing Point Depression and Boiling Point Elevation and Osmosis - *CC BY-NC-SA 4.0*
    - 5.4 Writing and Balancing Chemical Equations - *CC BY-NC-SA 4.0*
        - 5.4a Example How Much Carbon Dioxide - *Undeclared*
    - 5.5 Limiting Reactant and Theoretical Yield and Percent Yield - *CC BY-NC-SA 4.0*
    - 5.6 Representing Aqueous Reactions Molecular and Ionic and Complete Ionic Equations - *CC BY-NC-SA 4.0*
    - 5.7 Chemical Reactions and Aqueous Reactions (Exercises) - *CC BY-NC-SA 4.0*
- 6: Reaction Kinetics - *CC BY-NC-SA 4.0*
    - 6.1: Chemical Kinetics - *CC BY-NC-SA 4.0*
    - 6.2 The Effect of Concentration on Reaction Rate - *CC BY-NC-SA 4.0*
    - 6.3: Reaction Mechanisms - *CC BY-NC-SA 4.0*
    - 6.4: The Effect of Temperature on Reaction Rate - *CC BY-NC-SA 4.0*
    - 6.5 Catalysts - *CC BY-NC-SA 4.0*
- 7: Equilibrium and Thermodynamics - *CC BY-NC-SA 4.0*
    - 7.1: The Concept of Dynamic Equilibrium - *CC BY-NC-SA 4.0*
    - 7.2 The Equilibrium Constant - *CC BY-NC-SA 4.0*
    - 7.3: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations - *CC BY-NC-SA 4.0*
    - 7.4 Predicting the Direction of a Reaction - *CC BY-NC-SA 4.0*
    - 7.5 Le Châtelier’s Principle: How a System at Equilibrium Responds to Disturbances - *CC BY-NC-SA 4.0*
    - 7.6: The First Law of Thermodynamics - *CC BY-NC-SA 4.0*
    - 7.7: Enthalpy: The Heat Evolved in a Chemical Reaction at Constant Pressure - *CC BY-NC-SA 4.0*
    - 7.8 Quantifying Heat - *CC BY-NC-SA 4.0*
    - 7.9: Entropy and the Second Law of Thermodynamics - *CC BY-NC-SA 4.0*
    - 7.10: Gibbs Free Energy - *CC BY-NC-SA 4.0*
    - 7.11 Gibbs Free Energy and Equilibrium - *CC BY-NC-SA 4.0*
    - What we are studying - *CC BY-NC-SA 4.0*
- 8: Acids and Bases - *CC BY-NC-SA 4.0*
    - 8.1: An Introduction to Acids and Bases - *CC BY-NC-SA 4.0*
    - 8.2: Brønsted-Lowry Acids and Bases - *CC BY-NC-SA 4.0*
    - 8.3 Lewis Acids and Bases - *CC BY-NC-SA 4.0*
    - 8.4: Acid Strength and the Acid Dissociation Constant (Ka) - *CC BY-NC-SA 4.0*
    - 8.5: Autoionization of Water and pH - *CC BY-NC-SA 4.0*
    - 8.6 - Finding the Hydronium Ion Concentration and pH of Strong and Weak Acid Solutions - *CC BY-NC-SA 4.0*
    - 8.7: The Acid-Base Properties of Ions and Salts - *CC BY-NC-SA 4.0*
    - 8.8: Buffers: Solutions That Resist pH Change - *CC BY-NC-SA 4.0*
    - 8.9 Buffer Capacity and Buffer Range - *CC BY-NC-SA 4.0*
    - 8.10: Lewis Acids and Bases - *CC BY-NC-SA 4.0*
    - 8.11: Acid/Base (Exercises) - *CC BY-NC-SA 4.0*
- 9: Electrochemistry - *CC BY-NC-SA 4.0*
    - 9.1: Oxidation-Reduction Reactions - *CC BY-NC-SA 4.0*
    - 9.2: Standard Reduction Potentials - *CC BY-NC-SA 4.0*
    - 9.3 Cell Potential, Gibbs Free Energy, and Equilibrium - *CC BY-NC-SA 4.0*
    - 9.4: Batteries: Using Chemistry to Generate Electricity - *CC BY-NC-SA 4.0*
    - 9.5 Driving Reactant-Favored Reactions Using Electricity - *CC BY-NC-SA 4.0*
    - 9.6 Undesirable Redox Reactions - *CC BY-NC-SA 4.0*
- Back Matter - *CC BY-NC-SA 4.0*
    - Index - *Undeclared*
    - Glossary - *Undeclared*
    - Detailed Licensing - *Undeclared*