ENVIRONMENTAL ENGINEERING COLLECTION

Francis J. Hopcroft, *Collection Editor*

Chemistry for Environmental Engineering

Armen S. Casparian

Gergely Sirokman

MOMENTUM PRESS
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DEDICATION

ASC wishes to dedicate this book to his three children, Meghan, Dara, and Brendan, who I hope read this book (and its companion volume) and satisfy some of their intellectual curiosity. I hope they go on to inspire others about environmental quality, be it in the workplace, at home, or in lands yet to be explored.

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PREFACE

Why another book on chemistry, or even chemistry for environmental engineering?

There is considerable concern and worry for the survival of our planet which necessarily means the survival of our species, the human race. Survival rests on sustainability. Sustainability depends on a balance of the three factors—world economy, global society, and the physical environment. Sustainability opposes growth for the sake of growth—the philosophy of the cancer cell. Put another way, not all change is progress. At this time, the world economy appears to be on a collision course with the physical environment.

Many observers are concerned that apex predators and the diversity of species are disappearing; coral reefs are dying in acidified oceans; glacial water supplies are melting and raising sea levels; and land is being deforested and desertified at incredible rates. The use of synthetic chemicals in manufacturing and commerce is increasing every year. Human ingenuity has solved many problems. Consider, for example, how efficient man has become at catching fish from the ocean, to the extent that it is depleting breeding stocks, leading to collapse of fish populations. This has required international legislation to regulate who can fish where and when, and how much can be legally caught. Does anyone know if these laws are being enforced? Who are the enforcing agencies? William Forster Lloyd, a 19th century mathematician who first developed the "Tragedy of the Commons," could be turning over in his grave.

Our civilization—location of our cities, the crops we grow, the technologies that underpin our industry and commerce—are based on a climate pattern that is rapidly changing. Scientific evidence is predicting that the Earth will become a warmer planet, sea levels will rise, precipitation patterns will shift causing many areas to suffer from drought while other areas to experience floods, and temperature extremes will become more common. Biodiversity will probably decrease, and new kinds of pests may develop and flourish, requiring new types of pesticides.

The physical environment means air and water quality and pollution, climate and its changes, energy production and consumption, and, ultimately, all of the Earth's resources. How they are interconnected and managed will determine changes in our lifestyles. Who will make these decisions?

To understand, maintain, and protect the physical environment, a basic understanding of chemistry, biology, and physics, and their hybrids is useful. Environmental engineers, perhaps more than any other single engineering group, will be relied upon to solve our problems, design solutions, and help escort us into a new "normal." But the wisdom and expertise of nonscientifically educated individuals will also be needed and equally treasured. This, then, is the motivation behind this book. We hope that individuals with interest from all disciplines and backgrounds will find this book readable and useful. As Mark Twain once observed, "History may not always repeat itself, but it sure does rhyme a lot."

ACKNOWLEDGMENTS

We also want to take this opportunity to thank Professor Francis Hopcroft, editor, colleague, and, more importantly, friend, who's unwavering support, insights, and leadership over many years helped inspire and complete this book.

We also owe Professor Laurie Grove a debt of gratitude for her thorough and insightful review of our work. This book could not be what it is without her input.

INTRODUCTION

Chemistry is a science that has become critical to the study of many different fields, and is applied on a regular basis to engineering problems, sometimes even without the users realizing they have done so. This text serves to remind those who have likely studied chemistry early in their careers as students, but have since, perhaps, forgotten some of the more explicit lessons of those courses, even if they retained the essential principles and concepts. Herein the authors present a recap of introductory chemistry, and organic and polymer chemistry basics, that are essential to the understanding of many engineering applications, especially important in environmental engineering. It is hoped that students in other fields of engineering and science will also find this book useful, particularly with the generous number of solved examples provided.

Chapter 1 presents the most fundamental principles of chemistry, the nature of matter, and the basics of chemical accounting. It is roughly the equivalent of a first semester introductory chemistry course. Every effort has been made to demystify the subject while maintaining its integrity.

In Chapter 2, more advanced topics, normally encountered in a second semester introductory course are discussed. These topics include equilibrium and the closely related topic of solubility, kinetics, thermodynamics, and electrochemistry. Relevant examples can be found here, as these topics often play key roles in environmental applications.

The last chapter of this text, Chapter 3, gives a recap of an organic chemistry structure course. The naming and structure of organic compounds are discussed. Of particular interest to the reader may be the sections discussing polymer chemistry, as modern construction and consumer products rely more and more heavily on plastics and adhesives that fall into this category of chemicals.

Finally, there is a companion book to this work, *Applied Chemistry for Environmental Engineering*. That book delves deeper into topics that may be of particular interest to environmental engineers, from the chemistry perspective. This book serves as a foundation in knowledge for full enjoyment of the second volume.

CHAPTER 1

FUNDAMENTALS OF CHEMISTRY I

1.1 INTRODUCTION: THE FUNDAMENTAL PROPOSITION OF CHEMISTRY AND MATTER

Chemistry is based on the premise that all matter is composed of some *combination* of 92 naturally occurring elements. Of these 92 elements, 11 are gases and two are known liquids at room temperature. Two others are solids but turn liquid at body temperature. The vast majority are solids and metals. The word "combination" is the key concept that gives chemistry its reputation of complexity. It may mean a single element or compound, or mixtures of elements, or mixtures of compounds, or mixtures of elements with compounds. Furthermore, mixtures may be subdivided into homogenous or heterogeneous. And to make matters even more complex, these systems of mixtures, if solutions, may exist as solids, liquid, or gases. Part of the challenge in chemistry, then, is to sort things out, organize, characterize, and identify them.

Chemistry is the branch of physical science that studies matter and the changes or "molecular rearrangements" it can undergo. These rearrangements, conventionally known as chemical reactions, involve the breaking of existing chemical bonds between atoms to form new bonds with other atoms. In the process, different molecules with different properties are formed. Electrons may be gained or lost, and energy changes generally accompany the reaction. Chemical reactions, as distinguished from nuclear reactions, involve the exchange of only electrons—never protons or neutrons. In a sense, chemistry is the recycling of atoms.

Visible evidence of chemical reactions includes the following:

- Bubbling or fizzing, indicating the release of a gas
- Color change

- Temperature change (heat released or absorbed)
- Formation of a precipitate
- Emission of light (chemiluminescence) or sound

Examples of common chemical reactions include the following:

- Rusting of iron or corrosion of any metal
- Generation of a current by a battery
- Combustion of fuel to produce energy
- Neutralization of excess stomach acid by an antacid
- Hardening of concrete

Chemistry also studies the structure of matter, including chemical and physical properties, correlating properties on the microscopic scale with behavior observed on the macroscopic scale. These can include properties such as vapor pressure, osmotic pressure, solubility, boiling and melting points, and energy and its transformations. Many of these properties may dictate or influence the outcome of a reaction.

There are actually four, conventional, physical states in chemistry: solid (s), liquid (l), gas (g), or aqueous solution (aq). The first three are regarded as pure, consisting of only a single substance. For example, $CaCl_2$ (s) would be pure solid calcium chloride, while $CaCl_2$ (l) would be molten calcium chloride (at a very high temperature). The fourth physical state, *solution*, is a homogenous mixture of uniform and constant composition, where a solute and a solvent can be identified and distinguished. [There are gaseous solutions, like air (oxygen dissolved in nitrogen), liquid solutions, like salt water (sodium chloride dissolved in water), and solid solutions, like gemstones (iron or chromium atoms regularly spaced in an aluminum oxide crystal).] Often referred to as the universal solvent, water is a ubiquitous substance on Earth and in the human body, and is the basis of all known life. Water-based (or aqueous) solutions are given the symbol (aq) inserted immediately after the chemical formula. Thus, an aqueous solution of calcium chloride would be written as $CaCl_2$ (aq), indicating that a given amount of solid calcium chloride was dissolved in a sufficient volume of water to make an aqueous solution. Note that water alone is a solvent, not a solution. The presence of the symbol (aq) always indicates a solute (usually a solid, but may also be another liquid or gas) dissolved in water, the solvent, to form a solution.

1.2 BASIC CONCEPTS: THE PERIODIC TABLE, SYMBOLS AND NOTATION, AND COMMON QUANTITIES AND THEIR UNITS

1.2.1 SYMBOLS AND NOTATION

A. As previously mentioned, chemistry is based on the premise that all matter is composed of some combination of the 92 naturally occurring elements. [Although the periodic table lists 118 elements, the final 26 are man-made or artificially synthesized, radioactive, and increasingly unstable, that is, they have short half-lives. They are not addressed in this chapter, but are discussed in Chapter 5 of "Applied Chemistry for Environmental Engineering," the companion volume to this book.] These elements are arranged in a particular order, known as **the periodic chart** or **periodic table,** in horizontal rows called **periods,** by increasing atomic number, and in vertical columns called **groups or families,** by similar electron arrangements or configurations, which give rise to similar chemical properties. **Electron configurations** are ordered arrangements of electrons based on specific housing rules. Energy levels or shells are quantized and exist from one to infinity. In the ground state of an atom, however, electrons can populate energy levels ranging from 1 to 7. Within each energy level or shell are subshells containing orbitals, the first four of which are labeled *s, p, d,* and *f.* Each of the four orbitals has a distinct shape and population limit: 1 *s* orbital with a maximum of 2 electrons; 3 *p* orbitals with a maximum of 6 electrons; 5 *d* orbitals with a maximum of 10 electrons; and 7 *f* orbitals with a maximum of 14 electrons.

B. Members of the same family are called **congeners,** especially important in organizing organic compounds such as polychlorinated biphenyls (or PCBs) or organochlorine pesticides. Here, the PCB molecule may have two, four, six, or eight chlorine atoms; all are congeners of the same family. Of more immediate relevance is the fact that some rows of the periodic table have names, such as the actinide (row 6) or lanthanide (row 7) series, while columns have names such as alkali metals (column 1A or 1), alkaline earth metals (column 2A or 2), transition metals (columns 3 through 12), halogens (column 7A or 17), and noble (inert) gases (column 8A or 18). The pure numeral system of identifying columns is more modern and preferred over the number and letter system.

C. Each element is symbolized by either a single capital letter or a capital letter followed by a single lowercase letter. Thus, the number of elements from which a compound is made up can easily be determined by counting the number of capital letters.

D. The **atomic number, *Z*,** of an element is the number of protons in the nucleus of its atom. The atomic number, which is always an integer and uniquely identifies the element, is written as a *left-hand subscript* to the element symbol, for example, ${}_{6}C$.

E. The **mass number**, **A**, of an element is the sum of the number of protons and number of neutrons in the nucleus, collectively known as the number of nucleons. Protons and neutrons are assigned a mass number of one atomic mass unit (amu) each, based on the carbon-12 atom as the standard. Although an element can have only one atomic number, it may have more than one mass number. This fact gives rise to the phenomenon of isotopes. **Isotopes** are atoms of the same element with the same atomic number but with a different number of neutrons. An element may have several isotopes, one or more of which may be radioactive and hence unstable. For example, oxygen has three naturally occurring isotopes, all of which are stable, while carbon also has three, one of which is radioactive. The mathematical average of all isotopic mass numbers of an element, weighted by the percent abundance in nature of these isotopes, constitutes the element's **atomic mass.** It is impossible to predict theoretically how many isotopes an element may have, or how many may be radioactive. The isotopes of a given element have almost identical chemical properties (i.e., reactivity) but different physical properties (i.e., density, melting point, etc.). The mass number is expressed as a *left-hand superscript* to the element symbol, for example, ${}^{12}C$.

F. In its elemental state, the electronic charge of an element is zero, that is, the number of electrons equals the number of protons. If an atom gains or loses electrons, it becomes charged. A charged atom is called an **ion.** A positively charged ion has lost one or more electrons and is called a **cation,** while a negatively charged ion has gained one or more electrons and is called an **anion.** The charge or oxidation state on the ion is expressed as a *right-hand superscript* to the element symbol, for example, Ca^{2+}.

G. Elements in a given vertical column are referred to as a group or family. The reason for this is that they have similar electron configurations and thus prefer to gain or lose the same number of electrons. This, in turn, helps predict their reactivity with other elements. There are eight major groups or families. For example, elements in the first two columns are known as alkali metals (starting with lithium and ending with francium) and alkaline earth metals (starting with beryllium and ending with radium), respectively. They prefer to lose one and two electrons from their outermost energy levels, respectively. They form cations, just as other metals do. Their ions are electron deficient; hence the number of protons outnumbers the number of electrons. Alkali metals are said to have a valence or oxidation state of +1, or are univalent, while alkaline earth metals are said to have a valence or oxidation state of +2, or are divalent. Meanwhile, elements in the next to the last column, known as halogens, are nonmetals. They prefer to gain one electron and form an anion, and have a valence or oxidation state of −1. Both the tendency for metals to lose one or more electrons and the tendency for nonmetals to gain one or more electrons are explained by their electron configurations and energy stabilization rules, and account for the respective reactivities. There is a large array of metals in the middle of the periodic table known as the transition metals. Because of their complex electron configurations, they have multiple, energetically stable, positive valences or oxidation states and form a variety of interesting, industrially useful compounds. The seven elements that lie in between metals and nonmetals that form a descending step in the periodic table are known as metalloids. They have the ability to both gain and lose electrons, depending on their immediate chemical environment; their properties are often less predictable but equally interesting. Consult Table 1.1 in the next section to see which elements form cations and which form anions, and which may form both.

In general, oxides of nonmetals, when dissolved in water, are acidic. Oxides of metals are alkaline or basic. Thus, substances such as calcium oxide or magnesium oxide are slightly alkaline in the presence of water. Substances such as carbon dioxide or sulfur dioxide, on the other hand, are slightly acidic. Normal rainwater, for example, has a pH of about 5.6 (slightly acidic) due to the presence of carbon dioxide in the atmosphere. For a distribution of important elements in the environment, see Table 1.8 at the end of this chapter.

H. **Free radicals** and **ions** may occasionally be confused with each other, but they are quite different and have different stabilities. Ions are electrically charged atoms, having gained or lost one or more electrons, for reasons discussed in the preceding paragraph, (G). They are quite stable in aqueous salt solutions. A list of common cations and anions is provided in Table 1.1.

Free radicals, on the other hand, concern unpaired electrons in electrically neutral molecules. Stable molecules are made when two atoms join together and form a bond in which two electrons are shared. This is a single bond and is consistent with the duet and octet rules for stable molecules. As will be seen in Chapter 3 in organic chemistry, double and triple bonds are also possible, in which four and six electrons are shared, respectively. In addition to bonding pairs, molecules may also have lone pairs of electrons, which do not participate in the bonding process, but serve to fulfill the octet rule for valence electrons. They also exist as pairs. However, occasionally, a molecule may exist in a metastable state having resonance structures (discussed in Chapter 3), where an atom has an unpaired electron. Such a molecule is referred to as a free radical, is highly reactive, and has a very short lifetime. One example of a free radical is the hydroxyl radical •OH [not to be confused with the hydroxide anion OH^-]. The equation below shows the reaction of hydroxyl radical with a methane molecule to produce a methyl radical, another free radical:

$$\bullet OH\ (g) + CH_4\ (g) \rightarrow \bullet CH_3\ (g) + H_2O\ (g)$$

From a health perspective, free radicals are known to react with DNA in the human body, leading to its unraveling and breakdown in coding operations and proper replication. Consumption of antioxidants, such as L-ascorbic acid (vitamin C), which preferentially react with free radicals, is believed to reduce this problem.

Example 1.1

Uranium, the element with atomic number $Z = 92$, has three naturally occurring isotopes: U-234, U-235, and U-238. Only U-235 is fissionable. When it combines with a halogen to form a compound, it commonly forms a cation with a +6 charge.

A. Using proper notation, write the symbol of the U-235 isotope, indicating its electronic charge (also known as the **valence** or **oxidation state**).
B. Determine the number of protons, neutrons, and electrons in one atom of this isotope.

Solution

A. The symbol, written with proper notation, is

$$^{235}_{92}\mathrm{U}^{6+}$$

B. The atom has 92 protons (note left-hand subscript).

It must also have 92 electrons, understood, in its neutral (uncharged) atom. However, since this atom has a charge of +6 (note right-hand superscript), it has *lost* six electrons to become positively charged. Hence, it now has only 86 electrons.

To compute the number of neutrons in this atom, subtract the atomic number (left-hand subscript) from the mass number (left-hand superscript): 235 – 92 = 143 neutrons.

1.2.2 COMMON QUANTITIES AND UNITS OF MEASUREMENT

Important, measurable quantities or variables, along with their symbols and common units of measurement, are as follows:

- **Temperature, *T***, in degrees centigrade or Celsius (°C), or in Fahrenheit (°F), or in Kelvin units (K).
- **Mass, *m***, in grams (g), or in kilograms (kg) (SI unit).
- **Amount, n, measured in moles,** one mole being 6.022×10^{23} particles (e.g., atoms, molecules, or formula units); see Section 1.4.
- **Molar Mass**, MM, the mass in grams of 6.022×10^{23} atoms of an element or molecules of a compound, that is, one mole of a substance; see Section 1.4. The terms **molecular weight** and **formula weight** are often used interchangeably with molar mass.
- **Avogadro's Number** or **Constant:** 6.022×10^{23} particles or items per mole.
- **Volume**, ***V***, in cubic centimeters (cm^3) or liters (L).
- **Pressure**, ***P***, in atmospheres (atm), pascal, tore, or psi.
- **Density**, ***d***, in grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL).
- **Concentration** may be expressed in any one of several units, depending on the application; see Section 1.7.

Note that amounts of substances are expressed in *grams* (unit of mass) or *moles. Liter* is a unit of volume.

1.3 WRITING CHEMICAL FORMULAS AND NAMES

1.3.1 INORGANIC NOMENCLATURE AND FORMULA WRITING

There are two methods to name inorganic compounds and write their chemical formulas:

1. The crisscross method for ionic compounds
2. The Greek prefix method for covalent compounds

To decide which method is suitable, it is first necessary to decide what class of compound is being named: **ionic** or **covalent.** Recall that ionic compounds are made up of a metal and a nonmetal, where one of more electrons has been effectively transferred from one atom to another. For example, salts, such as sodium chloride or potassium sulfide, are ionic compounds. Covalent compounds are made up of two nonmetals; examples are carbon dioxide and phosphorus pentachloride. Covalent compounds are characterized by covalent bonds, in which electrons are shared between two atoms. If the sharing is unequal, the bond is said to be **polar-covalent,** and one end of the molecule has a partial negative charge. Such molecules are referred to as **dipolar** and have dipole moments, which are quantitative measures of their polarity. [Higher order polarities, like quadrupoles (e.g., CO_2) and hexadecapoles (e.g., SF_6) do exist and can be calculated but are usually small and make an insignificant contribution to the net polarity.] If the sharing is equal, the bond is said to be nonpolar covalent; the molecule has no charge separation and hence no positive or negative end.

If the compound in question is ionic, use the crisscross method of nomenclature. Write the symbols of metal and nonmetal elements side by side (recall that a nonmetal ion may be a single anion or a polyatomic oxoanion, such as sulfate or nitrate), along with their respective valences or oxidation states as right-hand superscripts. Then crisscross the superscripts, that is, interchange them for the two elements, and write them as subscripts, omitting the plus or minus signs. If the two subscripts are the same, drop them both. In nomenclature, the name of the metal element is given first and that of the nonmetal element second, changing it to an "-ide" ending, such as chlor<u>ide</u> or sulf<u>ide</u>, or using the name of the oxoanion, like sulfate or nitrate.

If a compound is covalent, the Greek prefix method is used. Here, knowledge of valences is unnecessary, but it is necessary to know the first 12 numbers in Greek: mono, di, tri, tetra, penta, hexa, hepta, octa, nona, deca, undeca, and dodeca. The proper Greek prefix then precedes each element in the formula. As above, the name of the second element takes on the suffix "-ide."

It should be remembered that many compounds have chemical names as well as common names. A compound generally has only one correct chemical name but may have more than one common name. For example, the compound $Ca(OH)_2$ has the chemical name calcium hydroxide; it may also be referred to commonly as slaked lime or hydrated lime.

Table 1.1. Names and symbols of simple cations and anions (Type I), cations with multiple oxidation states (Type II), and polyatomic/oxoanions

Common Simple Cations and Anions

Cation Symbol	Name	Anion Symbol	Name
H^+	hydrogen ion	H^-	hydride
Li^+	lithium ion	F^-	fluoride
Na^+	sodium ion	Cl^-	chloride
K^+	potassium ion	Br^-	bromide
Cs^+	cesium ion	I^-	iodide
Be^{2+}	beryllium ion	O^{2-}	oxide
Mg^{2+}	magnesium ion	S^{2-}	sulfide
Ca^{2+}	calcium ion	N^{3-}	nitride
Ba^{2+}	barium ion		
Al^{3+}	aluminum ion		
Ag^+	silver ion		
Zn^{2+}	zinc ion		
Cd^{2+}	cadmium ion		

Common Type II Cations

Ion	Systematic Name	Older Name
Fe^{3+}	iron(III)	ferric
Fe^{2+}	iron(II)	ferrous
Cu^{2+}	copper(II)	cupric
Cu^+	copper(I)	cuprous

(*Continued*)

Ion	Systematic Name	Older Name
Co^{3+}	cobalt(III)	cobaltic
Co^{2+}	cobalt(II)	cobaltous
Sn^{4+}	tin(IV)	stannic
Sn^{2+}	tin(II)	stannous
Pb^{4+}	lead(IV)	plumbic
Pb^{2+}	lead(II)	plumbous
Hg^{2+}	mercury(II)	mercuric
Hg_2^{2+}	mercury(l)	mercurous

Names of Common Polyatomic Ions

Ion	Name
NH_4^+	ammonium ion
NO_2^-	nitrite ion
NO_3^-	nitrate ion
SO_3^{2-}	sulfite ion
SO_4^{2-}	sulfate ion
HSO_4^-	hydrogen sulfate ion (bisulfate ion commonly used)
OH^-	hydroxide ion
CN^-	cyanide ion
SCN^-	thiocyanate ion
PO_4^{3-}	phosphate ion
HPO_4^{2-}	hydrogen phosphate ion
$H_2PO_4^-$	dihydrogen phosphate ion
AsO_4^{3-}	arsenate ion
CO_3^{2-}	carbonate ion
HCO_3^-	hydrogen carbonate ion (bicarbonate ion commonly used)
ClO^-	hypochlorite ion
ClO_2^-	chlorite ion

(*Continued*)

Ion	Name
ClO_3^-	chlorate ion
ClO_4^-	perchlorate ion
CH_3COO^- or $C_2H_3O_2^-$	acetate ion
MnO_4^-	permanganate ion
$(COO)_2^{2-}$	oxalate ion
$Cr_2O_7^{2-}$	dichromate ion
CrO_4^{2-}	chromate ion
O_2^{2-}	peroxide ion

Note: The following halogens can form polyatomic ions in the same manner as chlorine:

BrO^-	hypobromite ion	IO^-	hypoiodite ion
BrO_2^-	bromite ion	IO_2^-	iodite ion
BrO_3^-	bromate ion	IO_3^-	iodate ion
BrO_4^-	perbromate ion	IO_4^-	periodate ion

Example 1.2

Write the correct chemical formula for each of the following compounds:

A. Calcium chloride
B. Aluminum sulfate
C. Iron (III) phosphate
D. Sulfur trioxide
E. Diphosphorus pentoxide

Solution

Compounds **A** to **C** are comprised of a metal and a nonmetal and are therefore ionic, so the crisscross method applies.

Compounds **D** and **E** are comprised of two nonmetals and are therefore covalent, so the Greek prefix method applies.

A. Calcium chloride: Ca^{2+} and Cl^- are the two ions (note that the numeral 1 in front of the minus sign in the chloride ion has been omitted because 1's are understood and not written).

Crisscrossing the superscripts 2 and 1 while omitting the signs gives $CaCl_2$.

Note that the subscript 1 next to Ca has been omitted because 1's are understood and are not written when specifying numbers of atoms.

B. Aluminum sulfate: Al^{3+} and $(SO_4)^{2-}$ are the two ions.

Crisscrossing gives $Al_2(SO_4)_3$.

Note that parentheses are necessary to express the fact that the subscript 3 refers to and thus multiplies both the sulfur and oxygen atoms (subscripts) inside the parentheses.

C. Iron (III) phosphate: Fe^{3+} and $(PO_4)^{3-}$ are the two ions.

Note that the iron (III) notation refers to the Fe^{3+} species, to be distinguished from the Fe^{2+} species, written as iron (II). This is the modern way of distinguishing the ferric ion from the ferrous ion. This same system of notation, using Roman numerals in parentheses, is used for all transition metals with multiple oxidation states.

Crisscrossing gives $Fe_3(PO_4)_3$.

Note that fine-tuning is necessary in this case. Since both subscripts are 3, they are omitted. Furthermore, the parentheses then become unnecessary and are dropped.

The fine-tuned answer is $FePO_4$.

D. Sulfur trioxide: S and O are the elements.

Sulfur is "mono" or 1 (understood and not written), and oxygen is "tri" or 3. Hence the formula is SO_3.

E. Diphosphorus pentoxide: P and O are the elements.

Phosphorus is "di" or 2, and oxygen is "penta" or 5. Hence the chemical formula is P_2O_5.

Example 1.3

Find the total number of atoms in one formula unit of compounds **A, B,** and **C** in Example 1.2.

Solution

In each case, the subscripts next to all the atoms in the formula unit are added together. Where parentheses are used, subscripts inside parentheses must first be multiplied by subscripts outside parentheses.

For $CaCl_2$:	1 Ca atom + 2 Cl atoms = 3 atoms total
For $Al_2(SO_4)_3$:	2 Al atoms + 3 S atoms + 12 O atoms = 17 atoms total
For $FePO_4$:	1 Fe atom + 1 P atom + 4 O atoms = 6 atoms total

Note: The percent oxygen (O) *by number* in $Al_2(SO_4)_3$ is 12/17 × 100 or 70.6%, while in $FePO_4$, it is 4/6 × 100 or 66.7%. Compare this calculation to the calculation for percent *by mass* in Example 1.6.

1.3.2 CALCULATING OXIDATION STATES FROM FORMULAS

Occasionally, it may be necessary to determine the oxidation state or valence of an ion in a compound from its formula. This situation is often encountered with compounds or polyatomic complexes containing transition metal ions, which may have multiple oxidation states. A simple algebraic equation solves the problem, as illustrated in Example 1.4.

Example 1.4

Find the oxidation state or valence of each underlined atom.

A. $K\underline{Mn}O_4$
B. $(\underline{Cr_2}O_7)^{2-}$

Solution

Here, it is necessary to know the oxidation states assigned to common "fixed" elements. Some guidelines include the following:

- Alkali metals are 1+.
- Alkaline earth metals are 2+.
- Oxygen is generally 2−.
- Halides are generally 1−.

Set up a simple algebraic equation based on the principle that the sum of known charges of individual atoms in the formulas, multiplied by their respective subscripts, must total the net charge on the formula unit of the compound or polyatomic ion.

A. For $KMnO_4$:

$$(1+)(1) + (x)(1) + (2-)(4) = 0$$

Note that x represents the unknown oxidation state of the Mn atom. The total is set to zero because the formula unit is electronically neutral or uncharged.

Solve for x: $x = +7$

Thus, the oxidation state of Mn in $KMnO_4$ is +7.

B. For $(Cr_2O_7)^{2-}$:

$$(x)(2) + (2-)(7) = -2$$

Note that the x represents the unknown oxidation state of the Cr atom. The total is set to −2 because the net charge on the complex is −2.

Solve for x: $x = +6$.

Thus, the oxidation state of Cr in $(Cr_2O_7)^{2-}$ is +6.

1.4 CALCULATING MOLAR MASSES AND AVOGADRO'S PRINCIPLE

The atomic masses are given for each element in the periodic table in *amus* or atomic mass units. The mass number of a given isotope of an element is the sum of the number of protons and the number of neutrons in its nucleus. Recall that in Example 1.1, the mass numbers of the three isotopes of uranium were given as U-234, U-235, and U-238. However, this is not equivalent to the atomic weight. Most elements have more than one isotope, so the natural distribution of the isotopes of an element must also be taken into consideration. Using the carbon-12 isotope as the standard for mass, atomic masses can then be assigned to all the elements. For each element, this number must be a number that is averaged over all of its isotopes according to their relative percent natural abundance. The atomic weight of an element, then, is the average atomic mass of all of the element's naturally occurring isotopes. The molecular mass then becomes the sum of the atomic weights comprising the molecule, according to the number of each kind of atom occurring in the molecule. In other words, the molecular mass is the sum of the weights of the atoms represented in a molecular formula. Molecular masses (also called molecular weights) are the masses of molecules, which consist of essentially covalent compounds, while formula masses (also called formula weights) are the masses of formula units, which are essentially ionic compounds. The unit, in either case, is the amu, but often converted to the more useful grams/mole, which has the same numerical value.

To get from the microscopic level to the macroscopic scale, a quantity known as "the mole" (abbreviated mol) is defined. A mole of items, regardless of size, shape, or color, all of which are assumed to be identical, is equal to 6.022×10^{23}. This is a constant and is referred to as Avogadro's number. When one mole of atoms of an element is collected, the atoms have a collective mass (*molecular mass* for a molecule, or a *formula mass* for a formula unit) in **grams**. For comparison sake, one dollar bill or one small paper clip has a mass of about 1 g. The more general term used to refer to either molecular mass or formula mass is **molar mass**.

Example 1.5

Compute the molar masses of carbon dioxide and calcium nitrate.

Solution

For CO_2: The atomic weight of carbon is 12.0 g/mol. The atomic weight of oxygen is 16.0 g/mol.

Hence, the molar mass of carbon dioxide = 12.0 g/mol × 1 + 16.0 g/mol × 2 = $\boxed{44.0\text{ g/mol}}$

For $Ca(NO_3)_2$: The atomic weight of calcium is 40.1 g/mol;
the atomic weight of nitrogen is 14.0 g/mol;
atomic weight of oxygen is 16.0 g/mol

$$\begin{aligned}\text{Hence, the molar mass of calcium nitrate} &= 40.1\text{ g/mol} \times 1 + 14.0\text{ g/mol} \times 2 + 16.0\text{ g/mol} \times 6 \\ &= \boxed{164\text{ g/mol}}\end{aligned}$$

1.5 DETERMINING THE PERCENT COMPOSITION OF A COMPOUND

It is often important to be able to compute the percent composition of a compound. This ability is valuable, for example, when comparing compounds such as fertilizers or mineral supplements to determine which fertilizer contains the most nitrogen per unit mass of fertilizer, or which mineral supplement contains the most calcium per unit mass of a tablet. This determination requires that the molar mass of each of the compounds in question be calculated first. It is assumed that the reader is familiar with calculating the molar mass of a compound from the atomic weights of the individual elements in the compound. Example 1.6 illustrates this method.

Example 1.6

Determine the percent composition, by mass, of each of the following compounds:

A. Calcium oxide, CaO (commonly known as lime or quicklime)
B. Calcium carbonate, $CaCO_3$ (commonly known as limestone)

Solution

A. For CaO, the percent composition must be a two-part answer, because two elements make up CaO. Its molar mass is 56.1 g/mol. Thus:

$$\%\text{Ca} = \frac{(\text{atomic weight of Ca})(\#\ \text{Ca atoms in1 formula unit})}{\text{molar mass of CaO}} \times 100$$

$$= \frac{(40.1\text{ g Ca})(1)}{56.1\text{ g CaO}} \times 100$$

$$= 71.5\%$$

$$\%\text{O} = \frac{(\text{atomic weight of O})(\#\ \text{O atoms in 1 formula unit})}{56.1\text{ g CaO}} \times 100$$

$$= \frac{(16.0\text{ g O})(1)}{56.1\text{ g CaO}} \times 100$$

$$= 28.5\%$$

B. For $CaCO_3$, the percent composition must be a three-part answer, because three elements make up $CaCO_3$. Its molar mass is 100.1 g/mol. In a similar fashion, then,

$$\%\ \text{Ca} = \frac{(40.1\text{ g Ca})(1)}{100.1\text{ g CaCO}_3} \times 100$$

$$= 40.0\%\ \text{Ca}$$

$$\%\ \text{C} = \frac{(12.0\text{ g C})(1)}{100.1\text{ g CaCO}_3} \times 100$$

$$= 12.0\%$$

$$\%\ \text{O} = \frac{(16.0\text{ g O})(3)}{100.1\text{ g CaCO}_3} \times 100$$

$$= 48.0\%$$

Note that CaO has a higher percent Ca content by mass than $CaCO_3$.

1.6 DETERMINING EMPIRICAL AND MOLECULAR FORMULAS FROM PERCENT COMPOSITION

It is frequently useful to determine the chemical formula of an unknown compound. One method is **combustion analysis.** If the unknown compound is known to contain at least carbon and hydrogen, heating a measured amount in the presence of excess oxygen, a process known as combustion, produces carbon dioxide and water, which can be collected and weighed individually. All of the carbon atoms are contained in the carbon dioxide, and all of the hydrogen atoms are contained in the water. Since 1 mole of carbon dioxide is equivalent to 1 mole of carbon atoms, the number of moles of carbon and hydrogen in the unknown compound can be determined. If oxygen is also present in the unknown, it is distributed over the carbon dioxide and water products; its mass can be found by difference and then converted to moles of oxygen in the original or unknown compound. The mass or moles of other elements, such as nitrogen and sulfur, which form known compounds with oxygen, can be determined in the same fashion.

Another method is known as **elemental analysis.** A measured amount of the unknown substance is heated until it decomposes into its constituent elements, which are collected and analyzed individually. This method is called **pyrolysis** which is the intense heating of a compound or mixture in the absence of oxygen. The percent composition by mass of the compound is obtained. Example 1.7 illustrates how percent composition data can be used to deduce the chemical formula and ultimately the identity of an unknown substance.

Example 1.7

The percent composition by mass of an unknown compound is 40.9% carbon, 4.57% hydrogen, and 54.5% oxygen. By a separate analysis, its molecular weight or molar mass is found to be 176 g/mol. Find the molecular formula for the unknown compound:

A. the empirical formula
B. the molecular formula

Solution

A. Recall that the empirical formula represents the smallest group or combination of atoms, in the proper ratio, of which the molecule is composed. Assume a 100-g sample to work with. Then the given percentages can be translated directly into grams as follows:

$$40.9 \text{ g C, } 4.57 \text{ g H, and } 54.5 \text{ g O}$$

Next, convert these masses to moles by dividing each one by its respective atomic mass:

$$40.9 \text{ g C}\left(\frac{1.00 \text{ mol C}}{12.01 \text{ g C}}\right) = 3.41 \text{mol C}$$

$$4.57\ \text{g H}\left(\frac{1.00\ \text{mol H}}{1.008\ \text{g H}}\right) = 4.53\,\text{mol H}$$

$$54.5\ \text{g O}\left(\frac{1.00\ \text{mol O}}{16.0\ \text{g O}}\right) = 3.41\,\text{mol O}$$

At this point, the chemistry is done, and one could write the empirical formula in principle, using the calculated numbers as the subscripts: $C_{3.41}H_{4.53}O_{3.41}$.

Chemical formula rules stipulate, however, that these subscripts must not only be in the proper ratio but also must be whole numbers (integers). The problem now is to find a mathematical technique to maintain the ratio but change the subscripts into integers. One way is to divide through by the smallest number:

$$C_{3.41/3.41}H_{4.53/3.41}O_{3.41/3.41} = C_{1.00}H_{1.33}O_{1.00}.$$

Only the 1.33 subscript is not an integer. This can be corrected by multiplying through by the factor 3:

$$C_{3.00}H_{4.00}O_{3.00}$$

or simply written as $C_3H_4O_3$

This, then, is the empirical formula.

B. To find the molecular formula, divide the molar mass by the empirical mass. This ratio should always be a whole number (to three significant figures). Then multiply each of the subscripts in the empirical formula by this factor to obtain the molecular formula.

The empirical mass of the above chemical formula ($C_3H_4O_3$) is calculated in the same way as a molar mass would be and equals 88.0 g/mol. Thus, the factor is:

$$\frac{\text{Molar Mass}}{\text{Empirical Mass}} = \frac{176\ \text{g/mol}}{88\ \text{g/mol}} = 2.00$$

Therefore, the correct molecular formula is $C_6H_8O_6$.

1.7 SOLUBILITY AND CONCENTRATION UNITS FOR AQUEOUS SOLUTIONS

Many chemical reactions and processes occur in the solution state where water is the solvent. Solubility of a substance is an important chemical property, since clearly, not all substances are soluble in water and can use water as a reaction medium. The term "soluble" deserves some clarification. When a salt such as sodium chloride is said to be soluble in water, it means that moderate, visible or measurable amounts will dissolve. Even sodium chloride has an upper limit of about 35 g per 100 mL of water at room temperature. And similarly, even sand or trichloroethylene will dissolve to a limited extent in water, especially if the volume of water is sufficiently large. So it is preferable to say that the salt calcium phosphate is slightly soluble instead of insoluble, though use of the latter term usually outnumbers the former. Solubility rules for most inorganic compounds in water are well known and are summarized in Table 1.2. For organic compounds, whether solid or liquid, it is best to consult the *Handbook of Chemistry and Physics* or Wikipedia. Solvents other than water, such as acetone, alcohol, or hexane, are usually listed as alternatives.

Table 1.2. General solubility rules of cations and anions

Soluble Compounds	**Insoluble Exceptions**
Compounds containing alkali metal ions (Na^+, K^+, Rb^+, Cs^+) and the ammonium ion (NH_4^+)	None
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)	None
Halides (Cl^-, Br^-, I^-)	Halides of Ag^+, Hg_2^{2+}, and Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Compounds	**Soluble Exceptions**
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), sulfides (S^{2-}), and chromates (CrO_4^{2-})	Compounds containing alkali metal ions and the ammonium ion
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion

Several units exist in chemistry to quantify concentrations of aqueous solutions. The reason for the great variety is that different applications and chemical formulas require different units. The term "concentration" always implies the existence of a **solute,** present as a gas, liquid, or solid, dissolved in a suitable **solvent** to form a **solution.** Unless otherwise specified, the solvent for liquid solutions is understood to be water—hence the designation “aqueous solution,” abbreviated as **(aq).** The common definitions and units are as follows:

Molarity, M = moles of solute/liter of solution.
Molality, m = moles of a solute/kilogram of solvent.
Mole fraction, X = number of moles of component i/total number of moles of all components.
Percent by mass/mass = mass of solute in grams/mass of solution in grams.
Percent by volume/volume = volume of solute in milliliters/total volume of solution in milliliters.

Example 1.8

A chemist wants to prepare 0.500 L of a 1.50 molar solution of sodium chloride. How does he do this?

Solution

It is important to note that the unit of molarity provides the basis of making water-based chemical reactions and their direct stoichiometric calculations much easier, since the unit of all stoichiometric coefficients in balanced chemical reactions is *the mole*. Thus, use is made of the simple but powerful relationship:

Moles of Solute = Volume of Solution (L) × Molarity (M).

For example, the number of moles in 100 mL of a 2.5 M NaCl solution involved in a chemical reaction would be: moles NaCl = (0.100 L) × (2.5 M) = 0.250 moles NaCl.

Example 1.9

Hospital saline solutions are often labeled as 1.25% KCl (aq) by mass. What does this mean, and how is this calculated?

Solution

Using the definition of **percent by mass/mass**, this means:

$$1.25 \text{ g of KCl (s)}/100 \text{ g of solution} \times 100 = 1.25\%$$

This solution is made by adding 1.25 g of KCl (s) to 98.75 g of water. Note that while masses of solutes and solvents are exactly additive, volumes of *different* solutions (with different densities) are not.

Example 1.10

A wine bottle has a label that reads 11.5% alcohol (i.e., ethanol) by volume. What does this mean, and how is this calculated?

Solution

Using the last definition above for Percent by volume/volume, this means:

$$11.5\ \text{mL}\ C_2H_5OH/100\text{mL of wine solution} \times 100 = 11.5\%$$

Since most wine bottles contain 750 mL of fluid, this would mean there are 86.25 mL of pure ethanol contained in a bottle of wine.

Conversion from one concentration unit to another may occasionally be necessary or useful. The "factor-label method" is the most efficient way to handle this. Note the following example.

Example 1.11

Find the concentration of sulfuric acid solution, H_2SO_4 (aq), used in car batteries, in molarity (M). The density of battery acid is about 1.265 g soln/mL soln (while pure sulfuric acid stock solution is 1.800 g/mL, for comparison), and it is 35.0% by mass H_2SO_4.

Solution

Start with the density figure and then proceed as follows:

$$1.265\text{g soln / mL soln}\left(\frac{1{,}000\ \text{mL soln}}{1.00\ \text{L soln}}\right)\left(\frac{35.0\ \text{g}\ H_2SO_4}{100\ \text{g soln}}\right)\left(\frac{1.00\ \text{mol}\ H_2SO_4}{98.0\ \text{g}\ H_2SO_4}\right)$$

$$= 4.52\frac{\text{mol}}{\text{L}} = 4.52\ \text{M}$$

Note the systematic cancellation of units from left to right to get to moles H_2SO_4 per liter (L) of solution on the right, that is, the unit of molarity, M. Other unit to unit conversions are performed in much the same way.

1.8 GAS LAWS

1.8.1 THE KINETIC MOLECULAR THEORY OF GASES

The fact that all gases behave similarly with change in temperature or pressure led to the kinetic molecular theory or model. It can be summarized as follows:

- All matter in the gas phase is composed of discrete, point particles called molecules.
- In the gaseous state, molecules are relatively far apart.
- The molecules of all substances in the gaseous state are in continuous, rapid, straight-line motion. This motion is in three dimensions and is often called translation.
- This continuous motion is a measure of the kinetic energy of the system.
- In addition to translation, molecules may also rotate and vibrate, depending on the type of external energy source they are subjected to. These are known as internal modes of energy, and are separate from its kinetic energy.
- Collisions between molecules are assumed to be perfectly elastic. This means that when molecules collide with one another or with the walls of a container, they rebound without any loss of kinetic energy.
- The average kinetic energy of the molecules is directly proportional to its temperature in Kelvins. All gases at the same temperature will have the same kinetic energy. Particles in a gas are assumed to exert no attractive or repulsive forces.

This leads to gases having the following general properties:

1. Gases exert pressure, which can be measured in any number of units, for example, pounds per square inch, atmospheres, pascals, newtons per square meter, and Torrs.
2 Gases are highly compressible (unlike liquids and solids).
3. Gases diffuse easily.
4. Gases expand upon heating, providing the pressure remains constant.
5. The pressure exerted by a gas increases with temperature, providing the volume is held constant.

1.8.1 WHAT IS AN IDEAL GAS?

The model or assumptions for an ideal gas is twofold. First, it is assumed that the molecules consist of perfect spheres and they take up no room or volume themselves when compared to the volume of the container they are in (sometimes referred to as excluded volume). The second is that the individual gas molecules do not see or attract one another. This model then leads to the **Ideal Gas Law**, which states:

$$PV = n\mathrm{R}T \tag{1.1}$$

where P is the pressure of the gas system, V is the volume of the container of the system, T is the temperature of the gas (assumed to be the same as the temperature of the system container), n is moles of gas, and R is the universal gas constant, given in several different units in Table 1.3.

This law or formula is easy to work with and accurately predicts the behavior of all the ideal gases (helium, argon, etc.) as well as some commonly encountered gases such as nitrogen and oxygen, the two chief components of air, at or near room temperature and pressure.

However, under conditions of high pressure or low temperature, gases do not behave ideally. There are two reasons for this deviation from ideal behavior. First, the molecules themselves have a definite volume and size, and so do occupy a significant fraction of the volume of the container under high pressure. This causes the volume of the gas to be greater than that *calculated* for an ideal gas. Hence, a subtractive correction factor—“B”—is necessary. B is a measure of the excluded volume of one mole of particles. Second, molecules are brought closer together, and hence attract one another more strongly, especially under conditions of high pressure or low temperature. Hence, an additive correction factor—“A”—is necessary. A is a measure of the attractive forces between particles. The van der Waals equation, equation 1.2, represents *real* gas behavior under either of these two conditions, and especially when both conditions prevail. It is mathematically more complicated and therefore more difficult to work with. The constants “A” and “B” may be looked up by gas identity in a table in a handbook. An abridged table of values is given in Table 1.4.

$$\left[P + n^2\mathrm{A}/V^2\right]\left[V - n\mathrm{B}\right] = n\mathrm{R} \tag{1.2}$$

Table 1.3. The universal gas constant “R” in various units

0.082057 L·atm/mol·K
1.987 cal/mol·K
8.3145 J/mol·K
8.3145 m^3·Pa/mol·K
62.364 L·torr/mol·K

Table 1.4. van der Waals equation constants for common gases and volatile liquids

Gas	A ($L^2 bar/mol^2$)	B (L/mol)
Argon	1.355	0.03201
Butane	14.66	0.1226
Carbon dioxide	3.640	0.04267
Carbon monoxide	1.505	0.03985
Ethanol	12.18	0.08407
Nitric oxide	1.358	0.02789
Nitrogen	1.370	0.0387
Nitrogen dioxide	5.354	0.04424
Nitrous oxide	3.832	0.04415
Oxygen	1.382	0.03186
Radon	6.601	0.06239
Sulfur dioxide	6.803	0.05636

Besides the ideal gas law and the van der Waals models, there are no fewer than 10 other models for predicting the behavior of gases under real conditions. For the most part, they are far more mathematically complex. However, these two models and their corresponding equations accurately predict the behavior of almost all gases and vapors under most operating conditions and still retain relative mathematical simplicity.

1.8.2 THE GENERAL GAS LAW

Boyle's law (the pressure of a gas is inversely proportional to its volume) and **Charles's law** (the volume of a gas is directly proportional to its temperature) are generally combined into a more useful form known as the **general gas law**, expressed as

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2} \tag{1.3}$$

It is understood that this law is valid only for a closed system in which the total number of gas molecules and hence the mass are constant. The general gas law can be applied to an individual gas (e.g., nitrogen or carbon dioxide) or a mixture of gases (e.g., air). It is assumed that the gas is ideal, that is, follows the ideal gas law (see next section) as its equation of state.

Pressures P and volumes V may be in any units as long as they are consistent. Temperature must be absolute and thus in Kelvins. The subscripts 1 and 2 represent the initial and final states or conditions, respectively, for each quantity.

Example 1.12

A fixed quantity of gas occupies a volume of 2.0 L at a temperature of 20°C and a pressure of 1.0 atm. Find the volume that this gas would occupy at 40°C and 1.75 atm.

Solution

The general gas law (equation 1.3) applies. This is a problem in which the volume of a gas must be calculated at a new or different temperature and pressure. The data given are

$$P_1 = 1.0\,\text{atm};\quad P_2 = 1.75\ \text{atm}$$

$$T_1 = 20°\text{C} + 273\ \text{K} = 293\ \text{K};\quad T_2 = 40°\text{C} + 273\ \text{K} = 313\ \text{K}$$

$$V_1 = 2.0\,\text{L};\quad V_2 = ?$$

Substitute these values in the general gas law, and solve for V_2.

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(1.0\ \text{atm})(2.0\ \text{L})(313\ \text{K})}{(1.75\ \text{atm})(293\ \text{K})} = 1.22\ \text{L}$$

1.8.3 THE IDEAL GAS LAW

The **ideal gas law,** known as the **equation of state** for ideal gases, is a very useful and powerful problem-solving tool. It relates the pressure, volume, and temperature of a quantity of a gas. An **ideal gas** is a gas in which every molecule behaves independently of every other molecule (there is an absence of any intermolecular forces) and has no excluded volume. It is represented by the ideal gas law stated earlier (equation 1.1):

$$PV = n\mathrm{R}T$$

where

P = the pressure in atmospheres, torr, millimeters of mercury, pounds per square inch, pascals, etc.
V = the volume in liters, cubic centimeters, etc.
n = the number of moles of gas = mass of gas in grams/molar mass in grams per mole $= \frac{m}{MM}$
T = the absolute temperature in Kelvin units
R = the universal gas constant in units consistent with the above values, that is, check Table 1.3.

The ideal gas law contains four variables and the constant R. Given any three, the fourth can be found. In addition, this law can be used to find the molar mass or molecular weight if the mass of a gas is given.

Note that the ideal gas law is valid for a single, individual gas. If a mixture of gases is present, the ideal gas law is valid for each individual gas. In other words, a separate calculation using this law can be made for each gas present. The pressure of each gas thus calculated represents a partial pressure in the mixture. The total pressure can then be calculated according to Dalton's law (see the next section). However, to reduce calculation steps, this law can also be used to represent the total gas mixture as well.

Example 1.13

Exactly 5.75 g of an unknown gas occupies 3.49 L at a temperature of 50°C and a pressure of 0.94 atm. Find the molar mass or molecular weight of the gas.

Solution

The ideal gas law (equation 1.1) has many applications. One of them is to determine the molar mass of a gas.

$$PV = nRT = \left(\frac{m}{MM}\right)RT$$

In this case, solve for MM.
The data given in the problem are:

$P = 0.94$ atm
R = 0.0821 L·atm/K·mol
$V = 3.40$ L
$T = 273 + 50°\text{C} = 323$ K
$m = 5.75$ g

Substitute this information in the above equation, and solve or MM:

$$\begin{aligned}\text{MM} &= \frac{mRT}{PV}\\ &= \frac{(5.75\ \text{g})(0.0821\ \text{L}\ \ \text{atm}/\text{K}\ \ \text{mol})(323\ \text{K})}{(0.94\ \text{atm})(3.40\ \text{L})}\\ &= 47.7\ \text{g}/\text{mol}\end{aligned}$$

1.8.4 DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of all the gases in the mixture. Each partial pressure is the pressure that the gas would exert if the other gases were not present.

$$P_{\text{total}} = \sum P_i = P_1 + P_2 + P_3 + \ldots + P_n \qquad (1.4)$$

This law is particularly useful when gases are collected in vessels above the surface of an aqueous or nonaqueous solution. In an aqueous solution, the partial pressure of water vapor may be subtracted from the total pressure to help determine the partial pressures of the other gases or vapors present. The percent composition of a gaseous mixture may then be calculated, based on Dalton's law. To calculate the composition of the *solution phase* (e.g., in mole fraction or mole percent), **Raoult's Law** (see equation 1.15) must be used.

1.8.5 GRAHAM'S LAW OF EFFUSION

Recall that kinetic molecular theory states that the average speed of molecules in motion can be approximated by the **root-mean-square speed, U_{rms}:**

$$U_{\text{rms}} = \sqrt{\frac{3RT}{MM}} \tag{1.5}$$

Diffusion is the migration and mixing of molecules of different substances as a result of a concentration gradient across a fixed space and random molecular motion. **Effusion** is the escape of gas molecules of a single substance through a tiny orifice (pinhole) of a vessel holding the gas. **Graham's law of effusion** states that the rates of effusion of two different gases escaping, A and B, are inversely proportional to the square roots of their molar masses:

$$\frac{\text{Effusion Rate}_{\text{A}}}{\text{Effusion Rate}_{\text{B}}} = \sqrt{\frac{MM_{\text{B}}}{MM_{\text{A}}}} \tag{1.6}$$

Note that, at a fixed temperature, the *effusion time* is inversely proportional to the effusion rate, while the *mean distance traveled,* as well as the *amount of gas effused,* is directly proportional to the effusion rate.

1.8.6 INTERMOLECULAR FORCES

Chemical bonds between two or more atoms in a molecule are referred to as **intramolecular forces.** They are generally categorized as ionic, covalent, or metallic. These are the bonds that are broken and reformed during a chemical reaction. Significantly lower in strength are **intermolecular forces.** Intermolecular forces are generally attractive forces that exist between and among molecules of all shapes, sizes, and masses. They exist in the gaseous, liquid, and solid phases, as well as in the solution phase, where water is acting as the solvent to hydrate the solute.

They are important to understand because they are directly related to macroscopic properties such as melting point, boiling point, vapor pressure and volatility, and the energy needed to overcome forces of attraction between molecules in changes of state. Just as important, they also help determine the solubility of gases, liquids, and solids in various solvents (i.e., whether two substances are soluble or miscible in each other) and in part explain or reflect the "like dissolves like" principle. They are also critical in determining the structure of biologically active molecules such as DNA and proteins.

The categories of intermolecular, attractive forces for neutral or uncharged molecules in order of increasing strength are:

- London dispersion forces—exhibited by all molecules
- Polar forces or interactions—exhibited by all asymmetric molecules
- Hydrogen bonding—exhibited by molecules containing O-H, N-H, or F-H bonds

More generally, however, these forces of attraction, including charged and uncharged species, can be usefully organized and expanded, again in order of increasing strength, as follows:

- London dispersion forces—important in nonpolar substances (substances having no permanent dipoles).
- Ion–dipole forces—important in salts (consisting of ions) dissolved in water (aqueous solutions), also referred to as "hydration forces"
- Dipole–dipole forces—important in polar, covalent substances, which have permanent dipoles
- Hydrogen bonding, important in O-H, N-H, and F-H interactions
- Ion–Ion forces—important for ions only, usually present in aqueous solutions

The term "van der Waals forces" refers to dipole-induced dipole interactions and are a special case of the more general term "London dispersion forces."

Note that the distance between the oxygen and hydrogen atom within the water molecule is about 100 pm (where *pm* represents *picometer*, which is 1×10^{-12} meters). This is an *intramolecular* distance. In contrast, the distance between the oxygen atom of one water molecule and the hydrogen atom of a neighboring water molecule is about 180 pm. This is the *intermolecular* distance, typical in a hydrogen bond, and is almost double the intramolecular distance.

For example, polar substances such as acetone (C_3H_6O) will dissolve in other polar substances such as methyl chloride (CH_3Cl) but not in carbon tetrachloride (CCl_4), a nonpolar substance. Some polar substances, such as ethanol (C_2H_3OH), will dissolve in water in all proportions, that is, are completely miscible, because of hydrogen bonding between the hydrogen atom of the ethanol molecule and the oxygen atom of the water molecule. The same is true of ammonia and hydrofluoric acid, where hydrogen bonding occurs. Note that dimethyl ether (C_2OH_6), an isomer of ethanol, does not undergo hydrogen bonding with water because of its different molecular structure, that is, an ether vs. an alcohol (see Chapter 3, Table 3.6—ethanol vs. dimethyl ether). Hexane (C_6H_{14}) will dissolve in octane (C_6H_{18}) because both substances are characterized by nonpolar bonds. Naturally, size (length) and shape (branching of the molecule) also play a role in solubility considerations, and it is often difficult to determine which factor is more important in predicting solubility between two substances.

The greater the forces of attractions between molecules in a liquid, the greater the energy that must be supplied to separate them. Hydrogen bonding is a key reason why low molecular weight alcohols have much higher-than-expected boiling points, that is, heats of vaporization, in comparison to nonpolar hydrocarbons like hexane.

1.8.6.1 Two Special Cases

The following two examples show the importance and relevance of intermolecular forces.

Case 1

Bubbles Can Disappear

An interesting problem presented itself to a mechanical engineer who was trying to spread a thin film of adhesive onto a flat plastic surface to bond with another flat surface. The adhesive used was a hexane-based polymer, and a pressurized air gun was used to spread it as evenly as possible through a spreading nozzle. However, each time it was spread, tiny bubbles randomly appeared in the adhesive, preventing a tight or perfect seal. The engineer eventually realized that this was due to the fact that air, which is composed of nitrogen and oxygen, has a finite solubility in hexane, since both are nonpolar substances. Recalling the nature of intermolecular forces and solubility, a rough rule of thumb is that "like dissolves like." When helium, an inert gas, was substituted for air in the delivery mechanism, the bubbles disappeared, and the seal was perfect. Helium has virtually no solubility in hexane.

Case 2

Supercritical Fluids "To the Rescue"

Supercritical fluids are versatile solvents because their properties vary significantly with changing temperature and pressure. A supercritical fluid can be made to dissolve or extract one component of a mixture without disturbing the others, simply by altering its temperature or pressure or both. Thus, it can be used to remove environmental contaminants such as diesel fuel, PCBs (polychlorinated biphenyls), or OCP (organochlorine pesticides) from soil. In this case, carbon dioxide subjected to pressures as high as 400 atm, works nicely to extract a variety of congeners of PCBs or

OCPs from soil. Carbon dioxide is now also the solvent of choice in the dry cleaning industry, having replaced carbon tetrachloride banned since 1978 and less toxic chlorinated hydrocarbons used until the late 1990s.

1.9 CHEMICAL REACTIONS

1.9.1 FIVE CATEGORIES OF CHEMICAL REACTIONS

The purpose of categorizing a chemical reaction is to help predict the product or products of the reaction. In general, a chemical reaction is a process of molecular rearrangements, in which atoms change partners. Atoms are not destroyed or created. Total mass is conserved, that is, the mass of all of the reactants before the reaction must equal the mass of all of the products after the reaction, although the physical or chemical states of individual substances may change. This mass-conservation requirement explains why all chemical reactions must be properly balanced to be quantitatively valid and useful. Energy changes also accompany reactions—energy is either liberated or absorbed—since existing chemical bonds are broken and new bonds are formed.

With the letters A, B, C, and D used to represent simple elements or polyatomic ions, the five categories of reactions are as follows:

- Combination or synthesis

$$\mathrm{A + B \rightarrow AB}$$

- Decomposition

$$\mathrm{AB \rightarrow A + B}$$

- Single replacement/displacement

$$\mathrm{A + BC \rightarrow AC + B}$$

- Double replacement/displacement

$$\mathrm{AB + CD \rightarrow AD + CB}$$

- Combustion (complete)

$$(\mathrm{CH})_x + \mathrm{O_2} \rightarrow \mathrm{H_2O} + \mathrm{CO_2}$$

The notation (g), (l), (s), or (aq) immediately following a reactant or product is often employed to designate the chemical state of the substance.

1.9.2 OXIDATION-REDUCTION OR RED-OX REACTIONS

Another class of reactions that cuts across all other reaction categories consists of **oxidation-reduction reactions.** Oxidation-reduction reactions ("red-ox") reactions are reactions in which one substance is oxidized while another is simultaneously reduced. The processes of oxidation and reduction can be defined as follows: Oxidation is the loss of electrons, while reduction is the gain of electrons. However, diagnostically speaking, a substance is oxidized or reduced, respectively, if any *one* of the following conditions is met:

Oxidation

- The substance loses electrons.
- The substance gains oxygen atoms.
- The substance loses hydrogen atoms.

Reduction

- The substance gains electrons.
- The substance loses oxygen atoms.
- The substance gains hydrogen atoms.

Red-ox reactions are actually formed by the addition of two half-reactions—an oxidation reaction and a reduction reaction. It is impossible to have an oxidation without reduction or reduction without oxidation in a red-ox reaction. If one substance is oxidized, then another must be reduced, and vice versa, in the total or net reaction.

For example, each of the following shows an *oxidation reaction:*

$$\begin{gathered}\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^{-} \\ \left[\text{Zn has lost 2 electrons.}\right]\end{gathered} \tag{1.7}$$

$$\begin{gathered}\mathrm{C} + \mathrm{O}_2 \rightarrow \mathrm{CO}_2 \\ \left[\text{C has gained 2 O atoms.}\right]\end{gathered} \tag{1.8}$$

And each of the following shows a *reduction reaction:*

$$\begin{gathered}\mathrm{Cu}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Cu} \\ \left[\mathrm{Cu}^{2+}\text{has gained 2 electrons.}\right]\end{gathered} \tag{1.9}$$

$$\begin{gathered} C + 2H_2 \rightarrow CH_4 \\ [\text{C has gained 4 H atoms.}] \end{gathered} \tag{1.10}$$

Each half-reaction also has an associated electromotive potential, measured in electron volts (eV) and found in electromotive potential tables. This topic is discussed more fully in chapter 2.8.

An interesting case of red-ox reactions is **disproportionation**. In this type of reaction, a single substance undergoes oxidation and reduction at the same time. An example of this is the disproportionation of Cl_2 gas placed in water as a disinfecting agent. The reaction proceeds as follows:

$$Cl_2\,(g) + H_2O\,(l) \rightarrow H^+(aq) + Cl^-(aq) + HOCl\,(aq)$$

Here, the initially neutral diatomic chlorine molecule has undergone both reduction to the chloride anion (Cl^-) and simultaneously to the chlorine cation (Cl^+) in the HOCl molecule, known as hypochlorous acid. The actual disinfection of bacteria is carried out by the Cl^+ ion present in HOCl, which is a strong oxidizing agent.

1.9.3 WRITING AND BALANCING CHEMICAL REACTIONS

A chemical reaction consists of a reactant side (the left) and a product side (the right) separated by an arrow, which indicates *yields* or *produces.* Reactants and products are present as elements or compounds and are represented by appropriate symbols, as discussed in Section 3.1. Reactions must be balanced before they can be used in calculations to provide quantitative information. Again, a symbol placed immediately after the element or compound designates its chemical state: (g) for gas or vapor; (l) for liquid; (s) for solid, powder, precipitate, or crystal; and (aq) for solution, where water is understood to be the solvent for the indicated solute.

The simplest balancing method is called *balancing by inspection*. Although this method is often interpreted to mean balancing by trial and error, three simple rules regarding the order of balancing should be followed:

1. Balance metal atoms or atoms of any element present in the greatest number first. Greatest number means the largest subscript next to the atom.
2. Balance nonmetal atoms second, in descending order of magnitudes by checking subscripts, as in step #1 above.
3. Balance hydrogen atoms next to last, and then oxygen atoms last.

Balancing means inserting integers, known as stoichiometric coefficients, in front of elements or compounds to ensure the same number of like atoms on both sides of the reaction. Balancing requires keeping track of every kind of atoms, not molecules, that appear in the reaction. Compare atoms of a particular species on the left (reactant) side of the arrow with atoms of the same species on the right (product) side of the arrow. Use of fractional coefficients, such as ½ or ⅓, is permitted as a temporary way of balancing atoms, particularly hydrogen and oxygen atoms. Be sure to multiply each coefficient by 2 or 3, respectively, to eliminate the presence of fractional coefficients in the final reaction. Subscripts of atoms in compounds are fixed by nature and cannot be altered to achieve balancing.

The following are examples of **balanced reactions**:

A. $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

B. $3CaCl_2(aq) + 2Na_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6NaCl(aq)$

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

D. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The following points regarding these four reactions are noteworthy:

1. (A) is an example of a single-replacement reaction.
   (B) is an example of a double-replacement reaction.
   (C) is an example of a combustion reaction.
   (D) is an example of a decomposition reaction.
2. Only (C) is an example of a **homogeneous reaction,** since all of the reactants and products are present in the same physical state—gaseous. The other three are **heterogeneous reactions,** since the reactants and products are present in more than one state.
3. (A) and (C) are also examples of oxidation-reduction reactions. In (A), Al is oxidized while HCl is reduced; HCl is the **oxidizing agent**, while Al is the reducing agent. In (C), C_4H_{10} is oxidized while O_2 is reduced; O_2 is the oxidizing agent, while C_4H_{10} is the **reducing agent.**
4. There are two, and only two, levels of interpretation of the stoichiometric coefficients that balance these reactions. Consider (C). On the microscopic or invisible level, the reaction states that 2 molecules of C_4H_{10} react with 13 molecules of O_2 to produce 8 molecules of CO_2 and 10 molecules of H_2O. On the macroscopic or visible level, the reaction states that 2 moles of C_4H_{10} [2 times the molar mass of C_4H_{10} = (2 mol)(58 g/mol) = **116 g**] react with 13 moles of

O_2 [13 times the molar mass of oxygen = (13 mol)(32 g/mol) = **416 g**] to produce 8 moles of CO_2 [8 times the molar mass of CO_2 = (8 mol)(44 g/mol) = **352 g**] and 10 moles of H_2O [10 times the molar mass of H_2O = (10 mol)(18 g/mol) = **180 g**]. In other words, the only two correct units of stoichiometric coefficients are molecules and moles. The unit grams can be obtained by the use of molar masses, as shown, but are not directly readable.

5. Note, from point #4 above, that in (C), mass is automatically conserved. The total mass of reactants is 116 g + 416 g = 532 g. The total mass of products is 352 g + 180 g = 532 g. The conservation of mass principle requires that this equality always occurs.

1.9.4 SIMPLE STOICHIOMETRY

The term "stoichiometry" refers to the mass relationships between two reactants, two products, or, more commonly, a reactant and a product. **Stoichiometry** depends on a balanced reaction, which is essential in predicting the amount of product generated by a given amount of reactant or, conversely, the amount of reactant required to generate a given amount of product. The method recommended is the **factor-label method**, illustrated in Example 1.14. This method was also used earlier in the solution to Example 1.11.

Example 1.14

Consider reaction (C) in the previous section, the complete combustion of butane with oxygen to produce carbon dioxide and water. Calculate the mass of carbon dioxide that can be produced from 816 g of butane, assuming oxygen is in abundant or unlimited supply.

Solution

Since the reaction is balanced, the solution may proceed by setting up three conversion factors, written in parentheses and arranged from left to right, multiplying the given mass of butane. Next, draw a connecting "tie" line between the **2** in front of the butane and the **8** in front of the carbon dioxide, since these are the only two substances of interest. This will form the basis of the middle conversion factor below. The first and third conversion factors are the molar masses of butane and carbon dioxide, respectively. Thus:

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

$$816\text{ g }C_4H_{10} \times \left(\frac{1.0\text{ mol }C_4H_{10}}{58.0\text{ g }C_4H_{10}}\right) \times \left(\frac{8.0\text{ mol }CO_2}{2.0\text{ mol }C_4H_{10}}\right) \times \left(\frac{44.0\text{ g }CO_2}{1.0\text{ mol }CO_2}\right)$$
$$= 2{,}480\text{ g }CO_2$$

The mass of water can also be determined in a separate but similar calculation. The "tie" line would be drawn between the **2** in front of butane and the **10** in front of water. And the molar mass of water is 18.0 g/mol, instead or 44.0 g/mol for carbon dioxide. Thus, the mass of water could be computed to be 1,266 g, or 1,270 g rounded to three significant figures.

Note that the total mass of all (i.e., both) products would be the sum of the mass of carbon dioxide (2,480 g) and the mass of water (1,270 g) which equals 3,750 g. Further, the principle of the conservation of mass stipulates that the total mass of all reactants must equal the total mass of all products; 3,750 g must also represent the total mass of all reactants. It follows that since the original mass of butane was given as 816 g, the mass of oxygen that reacted must be 3,750 g – 816 g = 2,934 g, or 2,930 g to three significant figures.

Consider reaction (B) from the previous section. It is one of thousands of reactions that occur in water. The reaction shows the precipitation of calcium phosphate when solutions of sodium phosphate and calcium chloride are mixed. This reaction can be written in three different ways. In its current form, it is written as a "molecular" reaction. It can also be rewritten in a more useful form called the **"total ionic"** equation, as follows:

$$3Ca^{2+}(aq) + 6Cl^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq)$$
$$\rightarrow Ca_3(PO_4)_2(s) + 6Na^+(aq) + 6Cl^-(aq)$$

The benefit of this form is that it shows all of the ions that are present in the aqueous state (i.e., hydrated by water), separate from those that are present in the solid state (or gaseous in another reaction), and gives a more accurate, detailed representation of the actual chemical species present in solution. It is known that calcium chloride and sodium phosphate are soluble in water and forms solutions because of the (aq) symbol written after them on the reactant side. The same is true of sodium chloride on the product side. It is also known that calcium phosphate is insoluble in water and thus precipitates because of the symbol (s) written after it on the product side.

Still a third way of writing this reaction equation is called the **"net ionic"** equation. In this form, all chemical species which exist identically on both sides of the reaction equation, cancel and are deleted from the equation. In this case, it means $6Na^+$ (aq) and $6Cl^-$ (aq). These ions are given the name **"spectator ions."** They are present in solution but are not necessary for the reaction to occur.

Hence, the following equation is left:

$$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$$

It is noteworthy that while spectator ions do not participate in the net reaction, their presence contributes to the overall ionic strength of the solution. If large enough, their presence can increase the solubility of an insoluble salt. The effect is referred to as the "uncommon ion" or "salt" effect.

1.9.5 AN ILLUSTRATIVE EXAMPLE OF A DECOMPOSITION REACTION—AN EXPLOSION

Nitroglycerin, $C_3H_5N_3O_9$, is a well-known, powerful, liquid explosive. The explosion of nitroglycerin falls under the category of a decomposition reaction. Examining its products, the number of molecules, and the physical states they are in, as well as the amount of heat energy released, labeled ΔH, explains its tremendous destructive power. The heat energy released is also known as the enthalpy of reaction which will be discussed in more detail in Section 1.9.9. Consider the balanced reaction for this decomposition below:

$$4C_3H_5N_3O_9(l) \rightarrow 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)$$

$$\Delta H^\circ = -5{,}678\ \text{kJ}$$

Note the following three points:

1. A liquid reactant changes (upon ignition or shock) into all gaseous products, requiring greater volume.
2. Four moles of reactant decompose into 29 moles of products, requiring more volume.
3. A tremendous amount of heat energy—5,678 kJ—is released (indicated by the negative sign of ΔH), heating the already gaseous products and forcing them to expand, which requires greater volume (i.e., increased temperature causes increased pressure at constant volume).

This problem underscores the importance of understanding several individual chemical principles at work simultaneously.

1.9.6 LIMITING REAGENTS

In many reactions, the reactants are not present in stoichiometric ratios. One of the reactants, called the **limiting reagent,** is present in short supply. This reactant determines the outcome of the reaction, that is, the maximum amount of any product of interest that can be generated. The other reactant or reactants are thus present **in excess.** In any reaction in which two or more reactants are present and their respective amounts are given, the limiting reagent must be identified before the maximum amount of any product can be calculated.

Example 1.15

In an experiment, 50 g of hydrogen gas and 50 g of oxygen gas are ignited to form water. Calculate:

A. The mass of the water formed
B. The mass of any hydrogen or oxygen that is left over or unreacted

Solution

First, write the balanced chemical reaction as follows:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Since the amounts of both reactants are given, one of the reactants may be the limiting reagent. To find which reactant is the limiting reagent, convert each mass given in grams into moles, and compare. Thus:

$$50.0 \text{ grams } H_2 \times \frac{1.0 \text{ mol } H_2}{2.016 \text{ g } H_2} = 24.8 \text{ mol } H_2$$

$$50.0 \text{ grams } O_2 \times \frac{1.0 \text{ mol } O_2}{32 \text{ g } O_2} = 1.56 \text{ mol } O_2$$

From the balanced reaction, it is clear that 2 mol of H_2 require 1 mol of O_2. Thus, 24.8 mol of H_2 would require 12.4 mol of O_2. However, only 1.56 mol of O_2 are actually present or available for reaction. Thus, O_2 is in short supply and is the limiting reagent. Also, H_2 is present in excess and will be left over after the reaction.

A. To find the mass of water produced, again apply the factor-label method, using the molar amount of O_2 present as the starting point.

$$1.56 \text{ mol } O_2 \times \frac{2 \text{ mol } H_2O}{1 \text{ mol } O_2} \times \frac{18.0 \text{ g } H_2O}{1.0 \text{ mol } H_2O} = 56.2 \text{ g } H_2O$$

B. To find the mass of H_2 left over, subtract the amount of H_2 reacted with O_2 from the total mass of H_2 initially present and available in moles, since O_2 is the limiting reagent.

24.8 mol H_2 initially present

$$\begin{array}{l} -3.12 \text{ mol } H_2 \text{ reacted} \left(\text{equivalent to } 2 \times 1.56 \text{ mol } O_2\right) \\ \hline 21.68 \text{ mol } H_2 \text{ left over or unreacted} \end{array}$$

Now convert moles of H_2 to grams H_2 using molar mass of H_2:

$$21.68 \text{ mol } H_2 \text{ left over or unreacted} \times \frac{2.016 \text{ g } H_2}{1.0 \text{ mol } H_2}$$
$$= 43.7 \text{ g } H_2$$

1.9.7 PERCENT YIELD

The result obtained in Example 1.15 A is the theoretically predicted maximum amount of water. In reality, the amount of water actually collected may, for at least two reasons, be somewhat less. First, some reactions may not go to completion but instead may reach an equilibrium condition. Second, other reactions may have more than one pathway and may produce secondary or tertiary products that compete with the main route. In a sense, the percent yield of a reaction is a measure of efficiency.

In either case, a **percent yield** may be computed as follows:

$$\% \text{ Yield} = \frac{\text{Actual yield(g)}}{\text{Theoretical yield(g)}} \times 100 \qquad (1.11)$$

Example 1.16

Suppose that, in Example 1.11, the actual mass of water collected or measured is 48.0 g. Compute the percent yield of the reaction.

Solution

$$\% \text{ Yield} = \frac{48.0 \text{ g}}{56.2 \text{ g}} \times 100 = 85.4\%$$

1.9.8 CONSECUTIVE AND SIMULTANEOUS REACTIONS

Reactions that are carried out one after another in sequence to yield a final product are called **consecutive reactions**. In **simultaneous reactions**, two or more reactants react independently of each other in separate reactions at the same time. Said differently, a reaction may have more than one pathway to produce a spectrum of products.

An example of a consecutive reaction involves the purification of titanium dioxide, TiO_2, the most widely used white pigment for paints. To free TiO_2 of unwanted colored impurities, it must first be converted into $TiCl_4$ and then reconverted into TiO_2.

$$2TiO_2(s)\ (\text{impure}) + 3C(s) + 4Cl_2(g) \rightarrow 2TiCl_4(g) + CO_2(g) + 2CO(g)$$

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s)(\text{pure}) + 2Cl_2(g)$$

Note that the $TiCl_4$ product in the first reaction becomes a reactant in the second. This is the connecting link. For example, one could ask how many grams of carbon are required to produce 1.0 kilogram of pure TiO_2. First, it must be realized that 1 mole of TiO_2 (pure) requires 1 mole of $TiCl_4$. Then 2 moles of $TiCl_4$ require 3 moles of carbon. In this way, using the factor-label method, a calculation with conversion factors can be set up, connecting TiO_2 (s) with C (s).

1.9.9 ENERGY CHANGE FOR EXOTHERMIC VS. ENDOTHERMIC REACTIONS

Exothermic reactions are reactions that produce or generate heat to the environment or surroundings. By convention, their ΔH values are always negative. Endothermic reactions, on the other hand, absorb heat from the environment or surroundings (Figure 1.1). Their ΔH values are always positive. Units of heat energy are usually in either kilojoules per mole (kJ/mole) or kilocalories per mole (kcal/mol). The ΔH value of a reaction is the difference in energy between the energy of the products and the energy of the reactants as shown in the energy reaction diagram. See Section 2.7 in Chapter 2 for further clarification.

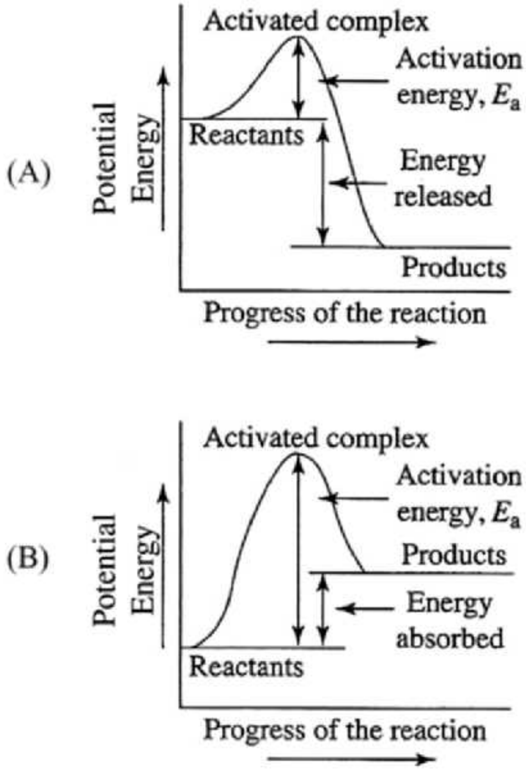

Figure 1.1. Change in potential energy for (A) exothermic reaction and (B) endothermic reaction

1.10 COLLIGATIVE PROPERTIES OF SOLUTIONS

1.10.1 BASIC CONCEPT

There are four colligative properties of solutions:

- Boiling-point elevation
- Freezing-point depression
- Vapor-pressure lowering
- Osmotic pressure

The term “colligative” means having to do with the *collection* or *number* of particles and/or ions dissolved in solution. It is an oversimplification, since size and polarity also play a role, albeit a less important one, in the chemistry of solutions. Colligative properties depend on the concentration of the solute (in units of molality) and its "*i*" factor (**van't Hoff factor**), that is, the total number of dissolved particles. The *"i"* factor depends on the specific chemical formula of the solute as well as the type of solute, as discussed below under "electrolytes."

Before describing each of the four colligative properties or effects in detail, it is useful to review the concept of a solution. Recall that a solution is a physical state wherein a solute has been dissolved completely and uniformly in a solvent, forming a solution of uniform composition. Unless specified otherwise, the solvent is assumed to be water, whose normal boiling point, freezing point, and density are well known. In the equations for each of the four properties, the concentration of the solution appears, although concentration units may vary. It is critically important, when doing calculations with solutions, to distinguish among units of mass, volume, and density for solute, solvent, and solution, respectively.

For solutions, there are three types of solutes or "electrolytes":

- Strong electrolytes
- Nonelectrolytes
- Weak electrolytes

Strong electrolytes are generally ionic compounds, such as salts, and strong acids and bases, that dissociate and ionize completely (i.e., 100%) in water. The solutions they form with water become strong conductors of electric currents. Examples include NaCl, KNO_3, $CaCl_2$, HCl, and NaOH. Thus, 1 mole of NaCl produces 2 moles of ions or particles; 1 mole of $CaCl_2$ produces 3 moles of ions or particles (1 mole of Ca^{2+} ions and 2 moles of Cl^- ions). The **van't Hoff factor** is the total number of ions or particles per formula unit or mole: 2.0 for NaCl, 3.0 for $CaCl_2$, and so on. Experimentally measured van't Hoff factors are generally less than theoretically predicted ones for a given solute.

Nonelectrolytes are generally alcohols and sugars, such as ethanol (C_2H_5OH) and glucose ($C_6H_{12}O_6$), or other organic substances that dissolve in water but do not ionize. One mole of a nonelectrolyte always produces 1 mole of particles. Thus, the van't Hoff factor is 1.0.

A weak electrolyte, such as acetic acid, is a substance that is only partially dissociated and ionized, typically 10% or less, leaving 90% or more undissociated and thereby behaving much like a nonelectrolyte. Its van't Hoff factor is greater than 1 but less than the total number of ions available for dissociation.

1.10.2 BOILING-POINT ELEVATION

When a nonvolatile solute is dissolved in water or another suitable solvent, the normal boiling point of the solvent is always raised. The amount of elevation in temperature, ΔT, is given by the equation

$$\Delta T = i\mathrm{K}_b m \tag{1.12}$$

where i = the van't Hoff factor (discussed above)
m = the molality of the solution
K_b = the ebullioscopic or boiling-point-elevation constant, characteristic of water (or other solvent) in °C·kg/mol. See Table 1.5 which lists K_b (and K_f) values for common solvents.

Example 1.17

What is the boiling point of a solution made by dissolving 70 g of NaCl in 300 g of water? The K_b for water is 0.512°C·kg/mol.

Solution

Use equation 1.12: $\Delta T = i\mathrm{K}_b m$, and note that $i = 2$ for NaCl. Then, molality,

$$m = \frac{\text{mol NaCl}}{\text{kg H}_2\text{O}}$$
$$= \frac{70\ \text{gNaCl/58.5g/mol}}{0.300\ \text{kg H}_2\text{O}} = 3.99$$
$$\Delta T = (2)(0.512)(3.99\text{mol/kg}) = 4.08\ ^\circ\text{C}$$
$$T_{\text{new}} = T_{\text{norm}} + \Delta T = 100\ ^\circ\text{C} + 4.08\ ^\circ\text{C} = 104.1\ ^\circ\text{C}$$

Table 1.5. Cryoscopic and ebullioscopic constants for common solvents

Substance	Freezing Point (°C)	Cryoscopic Constant (K·kg/mol)	Boiling Point (°C)	Ebullioscopic Constant (K·kg/mol)
Acetic acid	16.6	3.90	118.1	3.07
Benzene	5.5	5.12	80.1	2.53
Camphor	179.8	39.7	204.0	5.95
Cyclohexane	6.4	20.2	80.74	2.79

(Continued)

Substance	**Freezing Point (°C)**	**Cryoscopic Constant (K·kg/mol)**	**Boiling Point (°C)**	**Ebullioscopic Constant (K·kg/mol)**
Diethyl ether	−114.3	1.79	34.5	2.16
Ethanol	−114.6	1.99	78.4	1.19
Water	0.0	1.86	100.0	0.512

1.10.3 FREEZING-POINT DEPRESSION

When a nonvolatile solute is dissolved in water or any other solvent, the normal freezing point of the solvent is always lowered or depressed. The amount of depression, ΔT, is given by the equation

$$\Delta T = i\mathrm{K_f}m \tag{1.13}$$

where i and m have the same definitions as in equation 1.11, and $\mathrm{K_f}$ is the cryoscopic or freezing-point depression constant in °C · kg/mol. See Table 1.5 for a list of $\mathrm{K_f}$ values for common solvents.

Example 1.18

The freezing-point depression equation is often used to find the molar mass of an unknown solute. Find the molar mass (also known as the molecular weight) of a substance when 1.14 g of it is dissolved in 100.0 g of liquid camphor, whose freezing point is lowered by 2.48 °C. $\mathrm{K_f}$ for camphor is 39.7 °C · kg/mol as given in Table 1.5.

Solution

Use equation 1.13: $\Delta T = i\mathrm{K_f}m.$ Assume that the unknown substance is an organic nonelectrolyte, since camphor is also an organic nonelectrolyte, and the principle of "like dissolves like" applies. Thus $i = 1$. Then,

$$\Delta T = 2.48\ ^\circ\mathrm{C} \text{ and } \mathrm{K_f} = 39.7\ ^\circ\mathrm{C \cdot kg / mol}.$$

First, solve for the molality, m:

$$\mathrm{m} = \frac{\Delta T}{i\mathrm{K_f}} = \frac{2.48\,^\circ\mathrm{C}}{(1)(37.9)} = 0.0625 \text{ mol/kg}$$

But

$$\mathrm{m} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{\text{grams solute/molar mass solute}}{\text{kg solvent}}$$

Solve for molar mass, MM, of solute:

$$\begin{aligned}\mathrm{MM} &= \frac{\text{g solute}}{(\text{kg solvent})(\mathrm{m})} = \frac{1.14\ \mathrm{g}}{(0.100\ \mathrm{kg})(0.0625)} \\ &= 182\ \mathrm{g/mol}\end{aligned}$$

This number can then be compared with a hopefully short list of potential unknown substances, whose molar mass, as determined by the chemical formula, best matches this number. Note that for this type of analysis, solvents are chosen which have a large K_f value to help minimize the relative error from experiment.

1.10.4 HENRY'S LAW

Henry's law, although not considered a colligative property, concerns the solubility of a gas in a liquid, most often water. The law states that the solubility, *S*, of a gas in a liquid is directly proportional to the partial pressure, *P*, of the gas above the liquid; it can be written as follows:

$$S = k_{\mathrm{H}} P \tag{1.14}$$

where k_H is called Henry's constant, and depends on the gas, the solvent, and the temperature. A table of values for k_H may be found in the *Handbook of Chemistry and Physics* as well as in many introductory textbooks on chemistry. A brief table of k_H values for common gases is given in Table 1.6. The law implies that, at constant temperature, doubling the partial pressure of a gas doubles its solubility. The reciprocal of Henry's constant may be used as a measure of the volatility of organic substances dissolved in water, albeit with a limited solubility in water.

Another interpretation of k_H is that it is a partition coefficient. It expresses the partitioning of a substance between two different phases. It is the ratio of the concentration of a gas in the solvent phase to that in the vapor phase. **Partition coefficients** are of great value in predicting the molar concentration of a substance such as a contaminant in an organic solvent in physical contact with an inorganic solvent as well as in air–soil or water–soil systems. Henry's law helps explain such phenomena as the bends experienced by deep-sea divers who surface too quickly and the carbonation of beverages in tightly capped bottles.

Table 1.6. Henry's law constants k_H for aqueous solutions at 25°C

Gas	Constant (Pa/(mol/L))	Constant (atm/(mol/L))
He	$282.7 \times 10^{+6}$	2,865
O_2	$74.68 \times 10^{+6}$	756.7
N_2	$155 \times 10^{+6}$	1,600
H_2	$121.2 \times 10^{+6}$	1,228
CO_2	$2.937 \times 10^{+6}$	29.76
NH_3	$5.69 \times 10^{+6}$	56.9

1.10.5 RAOULT'S LAW FOR VAPOR-PRESSURE LOWERING

Raoult's law states that when a nonvolatile solute is added to water or another solvent, forming a solution, the vapor pressure of the solvent is depressed. In other words, the vapor pressure of the solution is lower than the vapor pressure of the pure solvent. The vapor pressure of the solution is directly proportional to the mole fraction of the solvent multiplied by the vapor pressure of the pure solvent:

$$P_{\text{soln}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} \tag{1.15}$$

where P_{soln} = the vapor pressure of the solution,

X_{solvent} = the mole fraction of the solvent $= \dfrac{\text{mol solvent}}{\text{mol solvent} + \text{mol solute}}$

$P^{\circ}_{\text{solvent}}$ = the vapor pressure of the pure solvent.

Vapor pressures are a measure of volatility. They may be expressed in any suitable units, such as atmospheres, millimeters of mercury, Torr, and pounds per square inch.

Note that Raoult's law applies to all ideal solutions. Ideal solutions mean systems where solute and solvent molecules have similar molecular structures or geometries and thus experience similar intermolecular forces (as in a benzene–toluene solution, a system of two structurally similar organic molecules, for example) *or* systems that are dilute solutions (where $X_{\text{solvent}} > 0.85$). For a binary system with only one solute and one solvent, Raoult's law may alternatively be expressed as follows:

$$P_{\mathrm{soln}} - P_{\mathrm{solvent}} = \Delta P = X_{\mathrm{solute}} P_{\mathrm{solvent}}{}^{\circ} \tag{1.16}$$

since

$$X_{\mathrm{solvent}} + X_{\mathrm{solute}} = 1 \tag{1.17}$$

Example 1.19

Calculate the vapor pressure at 100 °C of a solution prepared by dissolving 10 g of sucrose, $C_{12}H_{22}O_{11}$, in 100 g of water.

Solution

This is a real solution that is dilute, so Raoult's law should apply.

$$P_{\mathrm{soln}} = X_{\mathrm{solvent}} P_{\mathrm{solvent}}{}^{\circ} = X_{\mathrm{H_2O}} P_{\mathrm{H_2O}}{}^{\circ} \tag{1.18}$$

where $P_{\mathrm{H_2O}}{}^{\circ} = 760$ Torr, since the normal boiling point of water is 100 °C, and its vapor pressure at that temperature must be equal to atmospheric pressure. On the other hand, the vapor pressures of pure solvents can always be looked up in tables. Table 1.7 shows the values of the vapor pressures of some common solvents at room temperature, 25 °C.

To find $X_{\mathrm{H_2O}}$, compute the number of moles of sucrose *and* the number of moles of water.

$$\text{moles of sucrose} = 10 \text{ g } \mathrm{C_{12}H_{22}O_{11}} \times \frac{1.0 \text{ mol } \mathrm{C_{12}H_{22}O_{11}}}{342.3 \text{ g } \mathrm{C_{12}H_{22}O_{11}}} = 0.0292 \text{ mol}$$

$$\text{moles of water} = 100 \text{ g } \mathrm{H_2O} \times \frac{1.0 \text{ mol } \mathrm{H_2O}}{18.0 \text{ g } \mathrm{H_2O}} = 5.55 \text{ mol}$$

Thus,

$$X_{\mathrm{H_2O}} = \frac{5.55 \text{ mol}}{5.55 \text{ mol} + 0.0292 \text{ mol}} = 0.9948$$

Finally,

$$P_{\mathrm{soln}} = (0.9948)(760 \text{ torr}) = 756 \text{ Torr}$$

Additionally,

$$\Delta P = 760 \text{ torr} - 756 \text{ torr} = 4.0 \text{ Torr}$$

Table 1.7. Vapor pressure of water as a function of temperature

Temperature (°C)	Vapor Pressure (Torr)	Temperature (°C)	Vapor Pressure (Torr)
0	4.6	27	26.7
5	6.5	28	28.3
10	9.2	29	30.0
15	12.8	30	31.8
20	17.5	31	33.7
21	18.7	32	35.7
22	19.8	33	37.7
23	21.1	34	39.9
24	22.4	35	42.2
25	23.8	—	—
26	25.2	100	760

Vapor pressure is a function of temperature. The dependence of the vapor pressure of a pure solvent on temperature is given by the **Clausius–Clapeyron equation**:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}{}^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.19}$$

where P_1 and P_2 are the vapor pressures at absolute temperatures T_1 and T_2, respectively, and must be in Kelvins, and $\Delta H_{\text{vap}}{}^{\circ}$ is the molar heat of vaporization of the pure solvent at its *normal* or *standard* boiling point.

When the molar heat of vaporization or the boiling point of a substance is unknown, a frequently useful, empirical approximation for many liquids, *if hydrogen bonding is unimportant,* is Trouton's rule:

$$\frac{\Delta H_{\text{vap}}{}^{\circ}}{T_b} = 85 \tag{1.20}$$

This ratio, expressed in joules per Kelvin, allows the calculation of either the standard molar heat of vaporization, $\Delta H_{\text{vap}}{}^{\circ}$, or the boiling point, T_b, when one or the other is known.

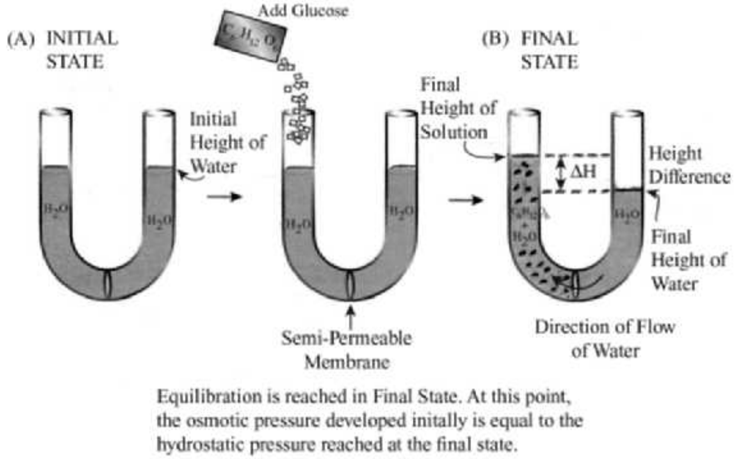

Figure 1.2. Three U-tubes showing the development of osmotic pressure. (A) System initially; (B) System after equilibrium is reached

1.10.6 OSMOTIC PRESSURE

Consider a U-tube in which a pure solvent such as water in the right arm is brought into contact with an aqueous solution made with a nonvolatile solute such as glucose (or any other soluble substance) in the left arm, and the two arms are separated by a semipermeable membrane (e.g., a selective membrane), permeable only to water, that is, solvent molecules. The two sides or arms of the U-tube are initially at the same height. It is observed that a pressure develops across the membrane that drives solvent molecules from the right arm into the left arm in an effort to dilute the solution and try to equalize concentrations in both arms. This pressure is called **osmotic pressure**, Π, and the process is known as osmosis (Figure 1.2). It is given by the equation:

$$\Pi = i\mathrm{MR}T \tag{1.21}$$

where
i = the van’t Hoff factor, which is equal to 1.00 since glucose is a nonelectrolyte,
M = the molarity of the solution,
R = the universal gas constant, 0.0821 L·atm/K·mol,
T = the absolute temperature in Kelvins.

Sometime later, the system in the U-tube reaches equilibrium, and a height differential, ΔH, between the solution level on the left and pure solvent level on the right is observed. Because of this height differential, a hydrostatic pressure, ΔP, develops and remains, and is given by the equation

$$\Delta P = \rho g \Delta H \tag{1.22}$$

where ρ = the density of the glucose solution, and g = the acceleration constant due to gravity.

In fact, the final hydrostatic pressure is equal to the initial osmotic pressure. Note the basic difference between osmosis and diffusion. Although both processes are driven by concentration gradients, a semipermeable membrane is present as a barrier in osmosis. No barrier is present in the process of diffusion.

Osmosis is a commonly occurring biological process, regulating and maintaining the proper concentrations of electrolytes in the cells of the human body. Osmometry is often used to find the molar mass (MM) of an unknown substance dissolved in solution through its molarity, M, when the other quantities—mass of unknown substance, volume of solution, temperature, and osmotic pressure—can be measured experimentally.

A calculation of osmotic pressure is shown in the following example.

Example 1.20

A very dilute sucrose solution of concentration 0.010 M in water is separated from pure water by an osmotic (i.e., semipermeable) membrane. Find the osmotic pressure that develops at 25 °C (298 K).

Solution

Use $\Pi = i\mathrm{M}\mathrm{R}T$, where $i = 1$ for sugar and all other nonelectrolytes.

So $\Pi = (1)(0.010\ \mathrm{M})(0.0821\ \mathrm{L\text{-}atm/K\text{-}mol})(298\ \mathrm{K}) = 0.24$ atm.

This result can also be converted into units of torr, if desired, since 1.0 atm = 760 Torr.

In that case, the osmotic pressure would be 182 Torr.

1.11 ACIDS, BASES, AND SALTS

1.11.1 BASIC CONCEPT

Substances known as acids and bases are commonly encountered and have important chemical properties. Therefore, this group of substances deserves separate treatment.

According to the **Arrhenius model**, an **acid** is any substance that, when dissolved in water, produces or causes to be produced hydrogen ions, H^+. A **base** is any substance that, when dissolved in water, produces or causes to be produced hydroxide ions, OH^-. The **Bronsted–Lowry model** stresses the fact that acids are *proton donors* and bases are *proton acceptors,* as well as the notion of *conjugate* (meaning "related") acids and bases. The **Lewis model** states that acids are substances that are electron-pair acceptors and bases are substances that are electron-pair donors. This concept broadens the meaning of acids and bases considerably to include many salts that would otherwise be excluded. Realistically, since a hydrogen ion is a bare proton, it is too reactive to exist as a stable species by itself. Hence, the real acid species is the hydronium ion, H_3O^+, a protonated water molecule, that is, $[H^+(H_2O)]$. Acids are powerful dehydrating agents.

When an acid and a base are added together, a neutralization (a double-replacement reaction) ensues, with water and a salt as the neutralization products. Quantitatively, one mole of acid, H_3O^+, exactly neutralizes one mole of base, OH^-. Thus, this is true for monoprotic acids and monobasic bases. Monoprotic acids contain one H^+ ion, such as HNO_3, while diprotic acids contain two H^+ ions, such as H_2SO_4, and thus require two OH^- ions to neutralize them. In general, polyprotic acids contain more than one ionizable H^+ ion; examples include phosphoric acid, H_3PO_4, with three H^+ ions, oxalic acid, $C_2O_4H_2$, with two H+ ions, as well as the aforementioned sulfuric acid.

Acids and bases may be strong or weak. This property is determined by molecular structure and is different from concentration. A strong acid is one that dissociates and ionizes completely or 100% into its hydrogen or hydronium ions and corresponding anions, known as its conjugate base. Similarly, a strong base is one that dissociates and ionizes completely into hydroxide ions and its corresponding cations, known as its conjugate acid. Weak acids and bases, in contrast, dissociate and ionize less than 100%, conventionally less than 10%, and typically less than 5%, into their respective ions. Recall that these substances are weak electrolytes, while strong acids and bases are strong electrolytes.

There are four common strong acids. All others can be assumed, by exclusion, to be weak.

- **Hydrochloric acid, HCl** [HBr and HI are also strong but uncommon; HF is weak.]
- **Nitric acid, HNO_3** [This is a *monoprotic acid* since it has only one hydrogen ion.]

- **Sulfuric acid, H_2SO_4** [This is a *diprotic acid* since it has two hydrogen ions.]
- Perchloric acid, $HClO_4$

Examples of common weak acids include acetic acid (in vinegar), boric acid (in the medicine cabinet), hydrofluoric acid (used as an agent to etch glass), ascorbic acid (vitamin C), carbonic acid, and phosphoric acid (the latter two in many carbonated beverages). Calculations for weak acids and bases are treated in Section 2.3 of Chapter 2.

Examples of strong bases are sodium hydroxide (NaOH) and potassium hydroxide (KOH). Examples of weak bases are ammonia, NH_3, which when dissolved in water becomes ammonium hydroxide, NH_4OH, and organic amines, such as methyl amine, CH_3NH_2.

When dissolved in water, **oxides of metals** (e.g., CaO, K_2O, MgO) undergo hydrolysis and are generally basic, while **oxides of nonmetals** (e.g., CO_2, SO_2, SO_3) also undergo hydrolysis and are generally acidic. Hydrolysis simply means reaction with water.

1.11.2 CONCENTRATION UNITS AND THE PH SCALE

Two units are routinely used to express concentrations of acids and bases:

- Molarity, M
- pH scale

Molarity is defined as the number of moles of H^+ ion for acids or of OH^- ion for bases per liter of solution. Concentration is symbolized by the use of brackets; that is, [ ] means moles per liter of the bracketed quantity.

The **pH**, representing the power of hydrogen ions, can be calculated from molarity. pH is useful for solutions whose acidic concentrations are less than 1.0 M, for example, 3.5×10^{-3} M.

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right] \qquad (1.23)$$

Equation 1.22 may also be written as follows:

$$\left[\mathrm{H}^+\right] = 10^{-\mathrm{pH}} \qquad (1.24)$$

Although not an absolute restriction, the pH scale conventionally runs from 0 to 14, because of the autoionization of water. Recall that K_w for water is 1.0×10^{-14} at 25 °C, since $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$.

Concentration of Hydrogen ions compared to distilled water	1/10,000,000	14	Liquid drain cleaner, Caustic soda	Examples of solutions and their respective pH
	1/1,000,000	13	bleaches, oven cleaner	
	1/100,000	12	Soapy water	
	1/10,000	11	Household Ammonia (11.9)	
	1/1,000	10	Milk of magnesium (10.5)	
	1/100	9	Toothpaste (9.9)	
	1/10	8	Baking soda (8.4), Seawater, Eggs	
	0	7	"Pure" water (7)	
	10	6	Urine (6) Milk (6.6)	
	100	5	Acid rain (5.6) Black coffee (5)	
	1,000	4	Tomato juice (4.1)	
	10,000	3	Grapefruit & Orange juice, Soft drink	
	100,000	2	Lemon juice (2.3) Vinegar (2.9)	
	1,000,000	1	Hydrochloric acid secreted from the stomach lining (1)	
	10,000,000	0	Battery Acid	

Figure 1.3. The pH of some common substances

The pOH may be analogously computed for basic solutions:

$$\text{pOH} = -\log\left[\text{OH}^-\right] \tag{1.25}$$

In addition, since

$$\text{pH} + \text{pOH} = 14 \tag{1.26}$$

it is always possible to find pOH from pH, or vice versa.

For the more commonly used pH, the **acid range** of solutions is **0 to 7,** while the **basic** or **alkaline** range is **7 to 14.** A pH of 7.0 represents a neutral solution such as distilled water. The pH values of common substances are shown in Figure 1.3.

Properties of acids include the following:

- They taste sour.
- They neutralize bases to produce water and a salt.
- They react with many metals to yield H_2 gas.
- They are strong dehydrating agents.

Properties of bases include the following:

- They taste bitter.
- They feel slippery.
- They react with fats and oil.
- They neutralize acids to produce water and a salt.

1.11.3 CALCULATIONS FOR STRONG ACIDS AND BASES

Examples 1.21 to 1.28 represent routinely encountered problems and calculations for strong acids and bases. In general, 1 mole of acid (H^+ ion) neutralizes 1 mole of base (OH^- ion) to produce 1 mole of water (H_2O).

Example 1.21

An aqueous solution of hydrochloric acid is 0.034 M. Find:

A. $[H^+]$
B. $[Cl^-]$

Solution

Since HCl is a strong acid, it dissociates and ionizes completely (100%) into its component ions. Thus,

A. $[H^+] = 0.034$ M
B. $[Cl^-] = 0.034$ M

It is safe to assume that [HCl] in terms of molecules is 0.

Example 1.22

For a 0.035 M HNO_3 solution, find:

A. $[H^+]$
B. pH

Solution

A. HNO_3 is a strong acid. Thus, a 0.035 M solution of HNO_3 yields 0.035 M H^+ ions (and 0.035 M NO_3^- ions), since there is a complete dissociation and ionization.
$[H^+] = 0.035$ M

B. $pH = -\log[H^+] = -\log(0.035 \text{ M}) = 1.46$

Example 1.23

Find $[OH^-]$ for the solution in Example 1.22.

Solution

Since this is an aqueous solution, the ion-product constant expression K_w for water applies:

$$\left[H^{+}\right]\left[OH^{-}\right] = K_{w} = 1.0\times10^{-14} \tag{1.27}$$

Thus,

$$\left[OH^{-}\right] = \frac{K_{w}}{[H^{+}]} = \frac{1.0\times10^{-14}}{0.035\,M} = 2.86\times10^{-13}\ M$$

This shows a very small OH^{-} ion concentration, but not zero, and illustrates the constant, reciprocal nature of H^{+} ions and OH^{-} ions.

Example 1.24

A sample of lemon juice has a pH of 2.4. Find its $[H^{+}]$.

Solution

Recall that $[H^{+}] = 10^{-pH}$. Thus:

$$\left[H^{+}\right] = 10^{-2.4} = 4.0\times10^{-3}\ M$$

Example 1.25

Find, for a 0.014 M solution of slaked lime, $Ca(OH)_2$:

A. $[OH^{-}]$
B. pH

Solution

A. The subscript 2 next to (OH^{-}) indicates that 1 mol of $Ca(OH)_2$ produces 2 mol of OH^{-} ions (along with 1 mol of Ca^{2+} ions).
It is assumed that $Ca(OH)_2$ is a strong base.
Thus,

$$[OH-] = 2(0.014\ M) = 0.028\ M$$

B. Furthermore, $pOH = -\log[OH^{-}] = -\log(0.028\ M) = 1.55$. Then,

$$pH = 14.0 - pOH = 14.0 - 1.55 = 12.45$$

Example 1.26: Acid-Base Reaction

A laboratory technician mixes 400 mL of a 0.125 M NaOH solution with 600 mL of a 0.100 M HCl solution. Find the pH of the resulting solution.

Solution

First compute the number of moles of acid and base to determine whether they are equal or, if not, which one is present in excess.

$$\begin{aligned}\text{Moles of H}^+ &= (\text{volume HCl})(\text{molarity HCl})\\ &= 0.060\,\text{mol}\end{aligned}$$

$$\begin{aligned}\text{Moles of OH}^- &= (\text{volume NaOH})(\text{molarity NaOH})\\ &= 0.050\,\text{mol}\end{aligned}$$

Since 0.06 mol of H^+ >0.05 mol of OH^-, the final solution will be acidic.

Furthermore, since 1 mol of acid reacts exactly with 1 mol of base, subtract moles of base from moles of acid to find the net moles of acid: 0.060 mol – 0.050 mol = 0.010 mol of H^+ left over or unreacted and present after mixing. This amount is in a total, combined volume of 1,000 mL or 1.00 L. Thus,

$$\left[\text{H}^+\right] = \frac{0.01\ \text{mol H}^+}{1.0\ \text{L}} = 0.01\ \text{M}$$

$$\text{pH} = 2.0$$

Example 1.27: Acid-Base Titration/Neutralization

A laboratory technician wishes to find the concentration of an unknown base. He performs a titration in which 42.50 mL of 0.150 M HCl exactly neutralizes 25.00 mL of the base. Determine the concentration of the unknown base.

Solution

Since moles of acid (A) equal moles of base (B) at the *endpoint* (point of neutralization), use the relationship

$$V_A M_A = V_B M_B \tag{1.28}$$

Solve for M_B:

$$M_B = \frac{V_A M_A}{V_B} = \frac{(42.50 \text{ mL})(0.150 \text{ M})}{25.00 \text{ mL}} = 0.255 \text{ M}$$

Example 1.28: Dilution of a Solution

A laboratory technician is asked to prepare 500 mL of a 0.750-M solution of HCl. The stock solution of HCl that she has is labeled 6.0 M. How much (what volume) should she take from the stock solution bottle?

Solution

The total number of moles of HCl ultimately desired in solution is:

$$\text{Moles of HCl} = V_{\text{HCl}}M_{\text{HCl}} = (0.500 \text{ L})(0.750 \text{ mol/L}) = 0.0375 \text{ mol}$$

This is the amount that must come from the 6.0-M solution. Since this amount is simply being redistributed from a concentrated solution (M_1 and V_1) to a more dilute one (M_2 and V_2), the number of moles of HCl in solution must remain constant. Thus, the number of moles of HCl *before* (1) must equal the number of moles of HCl *after* (2). So the calculation goes as follows:

$$\text{M}_1V_1 = \text{M}_2V_2 \tag{1.29}$$

Solve for V_1, substituting the values:

$$V_1 = \frac{(0.750 \text{ M})(0.500 \text{ L})}{6.0 \text{ M}} = 0.0625 \text{ L} = 62.5 \text{ mL of stock solution}$$

This same strategy can be applied to *any* dilution problem.

Supplemental Tables of Interest

Table 1.8. Common elements and their relative percent abundance in the Earth's (A) atmosphere, (B) hydrosphere, (C) biosphere, and (D) lithosphere

(A) Relative Atomic Abundance of Elements in the Atmosphere

Element	Percent by Number (%)
Nitrogen	78
Oxygen	21
Argon	0.93
Carbon dioxide	0.039

(B) Relative Atomic Abundance of Elements in the Hydrosphere

Element	Percent by Number (%)
Hydrogen	66.2
Oxygen	33.2
Chlorine	0.3
Sodium	0.3

(C) Relative Atomic Abundance of Elements in the Biosphere

Element	Percent by Number (%)
Hydrogen	49.7
Oxygen	24.9
Carbon	24.9
Nitrogen	0.3

(D) Relative Atomic Abundance of Elements in the Lithosphere

Element	Percent by Number (%)
Oxygen	61.1
Silicon	20.4
Aluminum	6.3

(*Continued*)

Hydrogen	2.9
Calcium	2.1
Sodium	2.1
Magnesium	2.0
Iron	1.5
Potassium	1.1
Titanium	0.2

(E) Relative Atomic Abundance of Metals in the Lithosphere

Metal	Percent by Number (%)
Aluminum	8.26
Iron	5.59
Calcium	4.12
Sodium	2.34
Magnesium	2.31
Potassium	2.07
Titanium	0.57
Other	<0.50

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CHAPTER 2

FUNDAMENTALS OF CHEMISTRY II

2.1 CHEMICAL EQUILIBRIUM

2.1.1 BASIC CONCEPT

Reaction equations describe substances, called reactants, which when put together, react and produce other different substances, called products. It may appear as if only products remain after the reaction is finished. In reality, many reactions do not go to completion, even if the reactants are present in stoichiometric ratios or amounts. Rather, they reach a condition known as equilibrium, denoted by double, reversible arrows in the reaction equation. **Equilibrium** means that there is a balance between the reactant side and the product side, or simply between the reactants and the products, and that the reaction is reversible. The chemistry of many air pollutants falls under the heading of equilibrium reactions. The equilibrium condition is dynamic, not static, allowing microscopic changes in reactant and product concentrations to take place, such that no net change in reactant or product concentrations occurs, provided that no external stresses are applied. At any given time, all species in the reaction equation—reactants and products—are present at equilibrium in varying amounts. The relationship among these varying amounts can be described by a mathematical formula known as the equilibrium constant expression or simply the equilibrium expression. The equilibrium expression is set equal to an equilibrium constant symbolized by K_c.

An equilibrium reaction can be generally represented as:

$$aA + bB \leftrightharpoons gG + hH \tag{2.1}$$

The K_c expression can then be expressed as:

$$K_c = \frac{[G]^g[H]^h}{[A]^a[B]^b} \tag{2.2}$$

where *a, b, g,* and *h* represent the stoichiometric coefficients in the balanced reaction, and the brackets [ ] indicate molar concentrations. The simplest interpretation of K_c is that it is a measure of the extent to which a reaction goes toward completion, that is, a reaction where the product side is favored. The meaning of K_c is discussed in more detail later in this section.

Four *points of caution* regarding the use of this expression are noteworthy:

- Only concentrations in units of molarity are permitted.
- Only species that have concentrations can appear. Thus, species in the solution state (aq) or in the gaseous state (g) are included, but species that are pure solids (s) or liquids (l) are not.
- K_c is a function of temperature (check the van't Hoff equation, equation 2.5, later in this chapter).
- All concentrations substituted into this expression must be taken at equilibrium.

A reaction in which all species are present in the same physical state (e.g., all gases or all solutions) is called a **homogeneous reaction,** while a reaction in which species are present in more than one physical state (i.e., mixed physical states) is called a **heterogeneous reaction.** If all species in a reaction are present in the gaseous state, an alternative form of the equilibrium constant expression can be written as K_p:

$$K_p = \frac{P_G{}^g P_H{}^h}{P_A{}^a P_B{}^b} \tag{2.3}$$

Here, *P* represents the partial pressure of each gas present at equilibrium. Any pressure unit is acceptable as long as it is consistent with the others and with the units of K_p, but atmospheres and torr are common.

A formula to convert K_c to K_p, and vice versa is as follows:

$$K_p = K_c(RT)^{\Delta n} \tag{2.4}$$

where

T = the absolute temperature in kelvins
R = the gas constant to be used in units consistent with partial pressure
Δn = the change in the number of moles of gas, that is, the total moles of product *minus* the total moles of reactant in the balanced reaction.

Example 2.1

Write the equilibrium constant expression K_c for the following reaction at 25°C:

$$2N_2O_5\,(g) \rightleftharpoons 4NO_2\,(g) + O_2\,(g)$$

Solution

Note that this is a homogeneous, gas-phase reaction. All three substances can have concentrations in units of molarity and should appear in the K_c expression:

$$K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

Given a value for K_c and asked to convert it to K_p, then, since all species are in the gaseous state, the equation would be:

$$\begin{aligned} K_p &= K_c(RT)^{\Delta n} \\ &= K_c(0.0821\ \text{L} \cdot \text{atm/K} \cdot \text{mol}\,298\ \text{K})^3 \\ \text{since } \Delta n &= (4+1)-2=3 \end{aligned}$$

Note that although the temperature is given, it is not used in the calculation. It may be useful in other calculations, however.

Example 2.2

Sulfur dioxide, SO_2 (g), is a common air pollutant. For the reaction

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

At 827°C, the value for K_c = 37.1. What is the value for the reverse reaction?

Solution

$$K_c\left(\text{reverse}\right)=\frac{1}{K_c(\text{forward})}=\frac{1}{37.1}=0.0269$$

2.1.2 THE MEANING OF K_c

Reactions with K_c values significantly greater than 1 (e.g., on the order of 10^4 or larger) approach completion, and their equilibria lie far to the right or the product side. In general, reactions that go to completion have exceptionally large or undefined K_c values. In contrast, reactions that have K_c values much less than 1 (e.g., on the order of 10^{-4} or smaller), as in the case of the K_a value of acetic acid discussed later in this chapter (see Section 2.3), do not undergo significant change. Their equilibria lie far to the left or the reactant side, and thus very little product forms. In the case of acids, the smaller the value of K_a, the weaker the acid. For reactions that have equilibrium constant values between 100 and 0.01, it can be said that significant concentrations of both reactants and products are present at equilibrium.

2.1.3 CALCULATIONS FOR K_c

A remarkable feature of the equilibrium constant expression is that K_c value for a given reaction at a given temperature are always constant and unique, regardless of which of the three approaches or pathways to equilibrium is followed:

- **Only** reactants present initially.
- **Only** products present initially.
- **Both** reactants **and** products present initially in a random ratio.

The K_c expression format, together with knowledge of the approach or pathway to equilibrium, can prove very valuable in developing a strategy to solving equilibrium problems, as shown in Examples 2.3 and 2.4.

Example 2.3

The reaction below is carried out in a 5-L vessel at 600 K. It is one way to convert carbon monoxide to carbon dioxide.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At equilibrium, it is found that 0.0200 mol of CO, 0.0215 mol of H_2O, 0.0700 mol of CO_2, and 2.00 mol of H_2 are present. For this reaction, calculate:

A. K_c
B. K_p

Solution

A. The reaction is balanced as it stands. All four substances are in the gaseous state and thus have concentrations that can be inserted into the K_c expression.

Since the *molar* amounts are given *at equilibrium,* each must be divided by the volume to convert it into molarity, and then substituted into the K_c expression. Thus,

$$\begin{aligned} K_c &= \frac{[CO_2][H_2]}{[CO][H_2 0]} \\ &= \frac{(0.0700 \text{ mol}/5.0 \text{ L})(2.00 \text{ mol}/5.0 \text{ L})}{(0.0200 \text{ mol}/5.0 \text{ L})(0.0215 \text{ mol}/5.0 \text{ L})} \\ &= 326 \end{aligned}$$

B. To convert to K_p, the conversion formula given in equation 2.4 is used:

$$K_p = K_c(RT)^{\Delta n}$$

Note that in this case, since

$$\Delta n = (1+1) - (1+1) = 0$$
$$K_p = K_c$$

In fact, $K_p = K_c$ whenever the product side and reactant side contain identical numbers of total moles.

Example 2.4

Ammonia gas, $NH_3(g)$, is introduced into a previously evacuated reaction vessel in such a way that its initial concentration is 0.500 M. The ammonia decomposes into nitrogen and hydrogen gases, according to the reaction given below, and eventually reaches equilibrium. The equilibrium concentration of nitrogen is found to be 0.116 M. Determine the value of K_c.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Solution

Knowing the approach or pathway to equilibrium is vital to solving this problem. It is clear in the statement that only reactant is present initially; therefore, all of the products are formed from the decomposition of NH_3. The equilibrium concentration of N_2 is given as 0.116 M. Because of the 3–to-1 stoichiometric ratio between H_2 and N_2, 3(0.116 M) = 0.348 M of H_2 must have also formed and is present at equilibrium.

Also, because of the stoichiometric ratio between NH_3 and N_2, 2(0.116 M) = 0.232 M of NH_3 must have decomposed. Thus, the concentration of NH_3 remaining and present at equilibrium is 0.500 M – 0.232 M = 0.268 M. Therefore, the values for the three species *at equilibrium* are as follows:

$$[NH_3] = 0.268 \text{ M}$$
$$[N_2] = 0.116 \text{ M}$$
$$[H_2] = 0.348 \text{ M}$$

Substitute these values in the K_c expression:

$$\begin{aligned} K_c &= \frac{[N_2][H_2]^3}{[NH_3]^2} \\ &= \frac{(0.116 \text{ M})(0.348 \text{ M})^3}{(0.269 \text{ M})^2} \\ &= 0.0681 \text{M}^2 \end{aligned}$$

2.1.4 PREDICTING EQUILIBRIUM USING A TEST QUOTIENT

It is often useful to know whether a reaction reached equilibrium, and, if so, under what conditions. This information can be obtained by measuring the concentrations of all species in the reaction and then determining a test quotient, *Q*. *Q* is identical in form to K_c, except that the values substituted in the expression may or may not be at equilibrium concentrations. The criteria for equilibrium are as follows:

- If $Q = K_c$, the reaction is at equilibrium.
- If $Q < K_c$, the reaction is not at equilibrium and needs to proceed to the right.
- If $Q > K_c$, the reaction is not at equilibrium and needs to proceed to the left.

Example 2.5

Consider the reaction given in Example 2.2 along with the following concentrations:

$$[SO_2] = 0.054\ \text{M}$$

$$[O_2] = 0.020\ \text{M}$$

$$[SO_3] = 0.012\ \text{M}$$

A. Is this reaction at equilibrium?
B. If not, in which direction will it proceed?

Solution

Write the expression for the test quotient Q, then substitute each of the three concentration values given into the expression:

A. $$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.012\ \text{M})^2}{(0.054\ \text{M})^2(0.020\ \text{M})}$$
$$= 247$$
Since $K_c = 37.1$, Q does not equal K_c. Thus, the reaction is not at equilibrium

B. Since $Q < K_c$, the reaction must proceed to the right to reach equilibrium.

2.2 STRESSES AND LE CHATELIER’S PRINCIPLE

Once a reaction has reached equilibrium, any external stress that is imposed results in a shift of the equilibrium and a subsequent change in the concentrations of the reactants and products involved. The direction of the shift—right (or product side) or left (or reactant side)—is in accordance with **Le Chatelier's principle,** which states that if a stress is imposed on a reaction at equilibrium, the reaction will shift either right or left in the way or direction that accommodates or relieves the stress.

There are five categories of stress:

- The reactant concentration or product concentration is increased or decreased.
- The temperature of the reaction is increased or decreased.
- The volume of the reaction vessel is increased or decreased.
- The pressure of the reaction is increased or decreased (in any one of three different ways).
- A catalyst is added to the reaction.

Example 2.6

Consider the following reaction already at equilibrium.

$$CS_2(g) + 3Cl_2(g) \rightleftharpoons S_2Cl_2(g) + CCl_4(g)$$

The enthalpy or heat of reaction is $\Delta H° = -84.3$ kJ.

Predict what will happen—increase, decrease, or no change—to the equilibrium concentration of CCl_4 when each of the following stresses is imposed:

A. Cl_2 is added.
B. S_2Cl_2 is removed.
C. The temperature is increased.
D. The volume of the reaction vessel is decreased.
E. The pressure is decreased by increasing the volume of the reaction vessel.
F. A catalyst is added.

Solution

Use Le Chatelier's principle to answer each part.

A. Adding Cl_2 will cause the reaction to shift to the right, increasing $[CCl_4]$.
B. Removing S_2Cl_2 will cause the reaction to shift to the right, increasing $[CCl_4]$.
C. To answer this part, the meaning of $\Delta H°$ must be understood. Recall the explanation provided in Section 1.9.9. This is the amount

of heat energy either liberated or absorbed in the reaction and may be expressed in either kilojoules (kJ) or kilocalories (kcal). If heat energy is liberated, the reaction is exothermic, and the sign of ΔH is negative by convention. If heat energy is absorbed, the reaction is endothermic, and the sign of ΔH is positive. Here, the sign is negative, so heat is produced. Hence, since raising the temperature adds heat and heat behaves as a product, increasing the temperature will shift the reaction to the left, decreasing [CCl_4].

D. In the balanced reaction, 4 molecules of reactant are reacting to form 2 molecules of product. Increasing the volume of the vessel favors the reactant or left side of the reaction, while decreasing the volume favors the product or right side. Hence, decreasing the volume will cause the reaction to shift to the right, increasing [CCl_4]. In the special case where the two sides of a reaction contain equal numbers of molecules, changing the volume has no effect.

E. If the pressure is decreased by increasing the volume, the effect can be evaluated as a volume stress. As discussed in **D**, increasing the volume will cause the reaction to shift to the left and decrease [CCl_4].

Note, however, that if the pressure is increased or decreased by the addition of a reactant or product (discussed in **A** or **B)**, the effect should be evaluated as a stress of the type discussed in A or B...

Also, note that if the pressure is increased by the addition of an inert or unreactive gas, there is no effect on the equilibrium.

F. A catalyst speeds up the rate of reaction. Since the reaction has already reached equilibrium, adding a catalyst will have no effect.

2.2.1 DEPENDENCE OF K_C ON TEMPERATURE

The exact dependence of K_c (or K_p) on temperature is given by the **van't Hoff equation:**

$$\ln\frac{K_c(2)}{K_c(1)}=\frac{\Delta H_{RX}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{2.5}$$

where $K_c(1)$ is the equilibrium constant value at absolute temperature T_1 and $K_c(2)$ is the value at T_2, ΔH_{RX} is the enthalpy (or heat) of reaction, and R is the gas constant in units of either joules per mole or calories per mole, consistent with the units of ΔH_{RX}. The similarity of the van't Hoff equation to the Clausius–Clapeyron equation, given as equation 1.18, is noteworthy.

2.3 CALCULATIONS FOR WEAK ACIDS AND BASES

In contrast to strong acids and bases, weak acids and bases dissociate and ionize into H^+ ions and OH^- ions, respectively, but to a very limited extent—normally less than 10% and more commonly less than 5%. The dissociation of weak acids and bases is another class or category of chemical equilibria. To be specific, for every 100 molecules of acid initially present, typically fewer than 5 molecules dissociate and ionize into hydrogen ions. Dissociate means "separate," and ionize means "form ions." Note that in gas-phase equilibrium reactions, reactants generally undergo only dissociation to form products. In solution-phase equilibrium reactions, as in weak acid or weak base equilibria, reactants not only undergo dissociation but also ionization. Weak acids produce few hydrogen ions, while weak bases produce few hydroxide ions. Their reactions can be characterized by an equilibrium acid (a) or base (b) constant, that is, K_a or K_b, respectively.

For example, acetic acid (found in vinegar) is a weak acid. Its equilibrium is represented as follows:

$$\mathrm{CH_3COOH(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + CH_3COO^-(aq)} \qquad (2.6)$$

Here, H_3O^+ is the active acid species, and CH_3COO^- is called the **conjugate base** of acetic acid. Recall the double arrows indicate an equilibrium process, meaning that this reaction does not go to completion and that all four chemical species in the reaction are present at any given time in various concentrations.

The equilibrium acid constant expression, K_a, is as follows:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} \qquad (2.7)$$

The K_a value for acetic acid at room temperature is 1.8×10^{-5}.

The average percent ionization, depending on initial concentration of the parent acid and temperature, is about 3% to 5%. Generally speaking, the smaller the value of the K_a, the weaker the acid. Table 2.1(A) gives K_a values for a number of weak acids at 25°C. It is evident then, from comparing

K_a values of acetic acid with nitrous acid, that acetic acid is weaker than nitrous acid. Phenol, in turn, is much weaker than either nitrous acid or acetic acid. Polyprotic acids have more than one hydrogen ion to dissociate and ionize, and so have more than one dissociation constant, that is, K_{a1}, K_{a2}, and K_{a3}, which get successively smaller, indicating progressive weakness in acidity. For example, oxalic acid has two K_a values, while citric acid has three.

Note that K_a values can also be expressed as pK_a values, just as hydrogen ion concentrations can be expressed as pH values, simply by taking the negative logarithm of the K_a value. See equation 1.22 in Chapter 1.11.2. Many references manuals compile weak acid dissociation constants as pK_a values.

Table 2.1. Equilibrium or dissociation constants for (A) weak acids, K_a (monoprotic and polyprotic) and (B) weak bases, K_b

	Monoprotic Acids		**K_a**
$HC_2O_2Cl_3$	Trichloroacetic acid	(Cl_3CCO_2H)	2.2×10^{-1}
HIO_3	Iodic acid		1.69×10^{-1}
$HC_2HO_2Cl_2$	Dichloracetic acid	(Cl_2CHCO_2H)	5.0×10^{-2}
$HC_2H_2O_2Cl$	Chloroacetic acid	(ClH_2CCO_2H)	1.36×10^{-3}
HNO_2	Nitrous acid		7.1×10^{-4}
HF	Hydrofluoric acid		6.8×10^{-4}
HOCN	Cyanic acid		3.5×10^{-4}
$HCHO_2$	Formic acid	(HCO_2H)	1.8×10^{-4}
$HC_3H_5O_3$	Lactic acid	$(CH_3CH(OH)CO_2H)$	1.38×10^{-4}
$HC_4H_3N_2O_3$	Barbituric acid		9.8×10^{-5}
$HC_7H_5O_2$	Benzoic acid	$(C_6H_5CO_2H)$	6.28×10^{-5}
$HC_4H_7O_2$	Butanoic acid	$(CH_3CH_2CH_2CO_2H)$	1.52×10^{-5}
HN_3	Hydrazoic acid		1.8×10^{-5}
$HC_2H_3O_2$	Acetic acid	(CH_3CO_2H)	1.8×10^{-5}
$HC_3H_5O_2$	Propanoic acid	$(CH_3CH_2CO_2H)$	1.34×10^{-5}

(*Continued*)

	Monoprotic Acids	**K_a**
HOCl	Hypochlorous acid	3.0×10^{-8}
HOBr	Hypobromous acid	2.1×10^{-9}
HCN	Hydrocyanic acid	6.2×10^{-10}
HC_6H_5O	Phenol	1.3×10^{-10}
HOI	Hypoiodous acid	2.3×10^{-11}
H_2O_2	Hydrogen peroxide	1.8×10^{-12}

	Polyprotic Acids	**K_{a2}**	**K_{a2}**	**K_{a3}**
H_2SO_4	Sulfuric acid	Large	1.0×10^{-2}	
H_2CrO_4	Chromic acid	5.0	1.5×10^{-6}	
$H_2C_2O_4$	Oxalic acid	5.6×10^{-2}	5.4×10^{-5}	
H_3PO_3	Phosphorous acid	3×10^{-2}	1.6×10^{-7}	
H_2SO_3	Sulfurous acid	1.2×10^{-2}	6.6×10^{-8}	
H_2SeO_3	Selenous acid	4.5×10^{-3}	1.1×10^{-8}	
H_2TeO_3	Tellurous acid	3.3×10^{-3}	2.0×10^{-8}	
$H_2C_3H_2O_4$	Malonic acid ($HO_2CCH_2CO_2H$)	1.4×10^{-3}	2.0×10^{-6}	
$H_2C_8H_4O_4$	Phthalic acid	1.1×10^{-3}	3.9×10^{-6}	
$H_2C_4H_4O_6$	Tartaric acid	9.2×10^{-4}	4.3×10^{-5}	
$H_2C_6H_6O_6$	Ascorbic acid	7.9×10^{-5}	1.6×10^{-12}	
H_2CO_3	Carbonic acid	4.5×10^{-7}	4.7×10^{-11}	
H_3PO_4	Phosphoric acid	7.1×10^{-3}	6.3×10^{-8}	4.5×10^{-13}
H_3AsO_4	Arsenic acid	5.6×10^{-3}	1.7×10^{-7}	4.0×10^{-12}
$H_3C_6H_5O_7$	Citric acid	7.1×10^{-4}	1.7×10^{-5}	4.0×10^{-7}

(*Continued*)

	Weak Bases	**K_b**
$(CH_3)_2NH$	Dimethylamine	9.6×10^{-4}
CH_3NH_2	Methylamine	4.4×10^{-4}
$CH_3CH_2NH_2$	Ethylamine	4.3×10^{-4}
$(CH_3)_3N$	Trimethylamine	7.4×10^{-5}
NH_3	Ammonia	1.8×10^{-5}
N_2H_4	Hydrazine	8.5×10^{-7}
NH_2OH	Hydroxylamine	6.6×10^{-9}
C_5H_5N	Pyridine	1.5×10^{-9}
$C_6H_5NH_2$	Aniline	4.1×10^{-10}
PH_3	Phosphine	10^{-28}

There are two ways to compute $[H^+]$ or $[H_3O^+]$ for a solution of a weak acid. If the percent ionization is given, multiply this by the initial concentration of the acid to obtain $[H^+]$. See Example 2.7. If the K_a value is given along with the *initial* concentration of the acid, equation 2.7 can be rearranged and solved for $[H_3O^+]$. See Example 2.8.

Example 2.7

A solution of 0.14 M nitrous acid, HNO_2, is 5.7% ionized. Calculate $[H^+]$.

Solution

Nitrous acid is obviously a weak acid, since its percent ionization is given as less than 10%, and certainly much less than 100%. Thus,

$$\left[H^+\right] = 5.7\% \times 0.14 \text{ M} = 7.98 \times 10^{-3} \text{ M}$$

Example 2.8

K_a for formic acid, HCOOH, contained in ant venom, is 1.80×10^{-4}. Find the pH of a solution that initially contains 0.200 mol of HCOOH in 500 mL of solution.

Solution

Since formic acid has a K_a value significantly less than 1.0, it must be a weak acid. Its equilibrium equation and K_a expression are as follows:

$$HCOOH(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + HCOO^-(aq)$$

$$K_a = \frac{[H_3O^+][HCOO^-]}{HCOOH} = 1.8 \times 10^{-4}$$

The strategy used in solving this type of problem is one that is commonly used in solving other equilibrium problems. The earlier expression for K_a equated to its value is a useful equation; it can be solved for $[H_3O^+]$, which can then be converted into pH.

The *initial* concentration of HCOOH is given as:

$$[HCOOH] = \frac{0.20 \text{ mol}}{0.500 \text{ L}} = 0.400 \text{ M}$$

However, all concentrations inserted into the K_a expression must be at equilibrium or final values. Therefore, let x be the number of moles per liter of HCOOH that dissociate and ionize into products. Since 1 mol of HCOOH produces 1 mol of H_3O^+ and 1 mol of $HCOO^-$, and all products come from only one reactant, ***at equilibrium,*** then:

$$[H_3O^+] = x$$

$$[HCOO^-] = x$$

$$[HCOOH] = 0.40 - x$$

Substitute these values in the K_a expression, equation 2.7:

$$\frac{(x)(x)}{0.40 - x} = 1.8 \times 10^{-4}$$

This is a quadratic equation in x. A simplifying assumption may be made. Since $x << 0.40$, it may be neglected in the denominator, reducing this to an easier-to-solve abridged quadratic equation. Then,

$$x^2 = (1.8 \times 10^{-4})(0.40)$$

$$x = 8.49 \times 10^{-3} \text{ M}$$

Thus,

$$\left[H_3O^+\right] = 8.49 \times 10^{-3}\ \mathrm{M}$$

Finally,

$$\mathrm{pH} = -\log[H_3O^+] = -\log(8.49 \times 10^{-3}\ \mathrm{M}) = 2.07$$

Note: A good rule of thumb to follow to determine whether the simplifying assumption is justified is as follows: Let M_a = initial molarity of acid; then,

$$\text{If } M_a / K_a > 100, \text{ then } M_a - x \cong M_a \text{ is a good approximation.}$$

The error incurred is usually about 1%, which is generally acceptable. The M_a/K_a ratio in this example produces a value of about 2,200. If the complete or unabridged quadratic equation is solved for this example, the calculated value for the equilibrium concentration of H_3O^+ is 8.57×10^{-3} M. Thus, the error incurred is about 0.93%, or slightly less than 1%.

2.3.1 HYDROLYSIS

Some compounds that appear neutral actually have acidic or alkaline properties. For example, when sodium acetate, $NaCH_3COO$, is dissolved in water, it reacts with water to form acetic acid (a weak acid) and a hydroxide ion. This process is called **hydrolysis,** and the resulting solution is slightly alkaline. Remember that the acetate ion is the conjugate base of acetic acid. Other basic salts in this category include sodium cyanide, potassium nitrite, and lithium carbonate.

Similarly, ammonium chloride, NH_4Cl, produces a slightly acidic solution when dissolved in water, again because of hydrolysis. Ammonium ion is the **conjugate acid** of ammonium hydroxide, and ammonia, NH_3, is the **conjugate base** of NH_4^+. Another salt in this category is aluminum chloride, $AlCl_3$. Gases such as CO_2 and SO_2 also undergo hydrolysis and produce H^+ ions and HCO_3^- and HSO_3^- ions, respectively.

Example 2.9

Calculate the pH of a 0.20 M solution of ammonium chloride, NH_4Cl.

Solution

NH_4Cl is the salt of a weak base, NH_3, and hence hydrolyzes when dissolved in water to form a slightly acidic solution.

$$NH_4^+(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + NH_3(aq)$$

The hydrolysis constant expression, K_h, can be expressed as follows:

$$K_h = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

The value for K_h is not given but can be found by applying the relationship

$$K_h = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

where K_b is the value of the equilibrium base constant for NH_3 in H_2O and is found in Table 2.1(B). It is analogous to K_a:

$$NH_3 + H_2O \leftrightharpoons NH_4^+ + OH^-$$

The same strategy is then used as in Example 2.8. At *equilibrium,* then,

$$\begin{aligned}\left[H_3O^+\right] &= x\\ [NH_3] &= x\\ \left[NH_4^+\right] &= 0.20 - x\end{aligned}$$

Therefore,

$$5.56\times10^{-10} = \frac{(x)(x)}{0.20 - x}$$

Use the same simplifying assumption as in Example 2.8, assume $x << 0.20$ M, and solve for x:

$$\begin{aligned}x^2 &= (0.20\,\text{M})(5.56\times10^{-10})\\ x &= 1.1\times10^{-5}\end{aligned}$$

Thus,

$$[H_3O^+] = 1.1 \times 10^{-5}\,M$$

And

$$pH = -\log\left[H_3O^+\right] = -\log\left(1.1\times10^{-5}\,M\right) = 4.96$$

The pH is less than 7.0, reflecting an acidic solution, as expected. *Note:* For the hydrolysis of an ion producing a *basic or alkaline* solution, $K_h = K_w/K_a$.

2.3.2 BUFFER SOLUTIONS AND THE HENDERSON–HASSELBALCH EQUATION

Buffer solutions are solutions that protect against large shifts in pH in the event of a shock due to the sudden addition of a strong acid or base. The pH of a buffer solution does, however, change slightly. Such a solution can be made with a combination of either

- A weak acid and its salt (conjugate base) or
- A weak base and its salt (conjugate acid).

Thus, acetic acid plus sodium acetate constitutes a buffer system, as does ammonium hydroxide plus ammonium chloride.

To determine the pH of a buffer solution, the **Henderson–Hasselbalch equation** may be used. In the case of a weak acid (e.g., CH_3COOH) and its conjugate base salt (e.g., $NaCH_3COO$):

$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{weak acid}]} \tag{2.8}$$

The buffering capacity of a system refers to the amount of acid or base it can absorb before its pH changes. Buffering capacity is generally at a maximum when [weak acid] = [conjugate base], so that $pH = pK_a$.

2.3.3 AMPHOTERISM

Amphoterism refers to the property of certain compounds to act as both acids and bases. For example, the compound $Al(OH)_3$, which is categorically a base, may react with acid to form $[Al(H_2O)_6]^{3+}$ and with excess base to form $[Al(OH)_4]^{-1}$. Both of these species are termed **complex ions** and are water soluble. They are governed by complex-ion equilibrium constants, as explained in Section 2.5 of this chapter. Aluminum oxide, Al_2O_3, is also amphoteric. The hydroxides as well as oxides of zinc(II) and chromium(III) are similarly amphoteric.

2.4 SOLUBILITY PRODUCT CONSTANTS

2.4.1 BASIC CONCEPT

Like the acids and bases discussed in the previous section, another group of substances comprised generally of ionic compounds that have very limited solubility in water deserves separate treatment. Examples include magnesium hydroxide (commonly known as milk of magnesia, an antacid), barium sulfate, (used in enemas to diagnose colonic tumors), and silver chloride. These substances are generally referred to as "insoluble" or "slightly soluble," and are governed by a solubility equilibrium expression and a solubility product constant known as K_{sp}, identical in concept to the principle of equilibrium discussed in Section 2.3.

The solubility of any salt depends on temperature. The solubility of most salts increases with increasing temperature. When a salt has dissolved to the maximum extent in a given volume of water at a given temperature, the solution is said to be **saturated.** Until that point is reached, the solution is **unsaturated.** If a saturated solution is heated above room temperature, more salt can be dissolved and be held in solution. If this solution is later slowly cooled (sometimes called *reversibly cooled*), it is possible to cool it back down to room temperature (or below), such that all of the dissolved salt can exist in the solution phase without precipitating out. Once this lower temperature is reached, the solution is said to be **supersaturated**. A sudden shock, for example, a mechanical disturbance, however, can cause instantaneous precipitation and the corresponding release of energy in the form of heat. The solubility of a salt is commonly measured in units of moles per liter, grams per liter, or milligrams per liter (often referred to as *parts per million* or simply *ppm*).

2.4.2 DEFINITION OF SOLUBILITY PRODUCT CONSTANT, K_{SP}

Consider, for example, the slightly soluble salt CaF_2 (s) in equilibrium with water. Its limited dissociation and ionization in water can be expressed as follows:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad (2.9)$$

And its solubility product constant, K_{sp}, as

$$K_{sp} = \left[Ca^{2+}\right][F^-]^2 \qquad (2.10)$$

Note that $[CaF_2 (s)]$ does not appear in the K_{sp} expression since it represents the undissolved portion and its pure solid. It has no concentration.

Also note that $[Ca^{2+}]$ represents the concentration of Ca^{2+} ion dissolved in the water, while $[F^-]$ represents the F^- ion concentration dissolved in the water.

Note also that when a given amount of CaF_2 (s) is dissolved in a known amount of water:

$$[Ca^{2+}(aq)] = 2\left[F^-(aq)\right] = [CaF_2(aq)]$$

where CaF_2 (aq) is that portion which is dissolved in water. In other words, whatever the proportion of CaF_2 (s) that dissolves in water, the same molar concentration is present as Ca^{2+} (aq) ion but twice that molar concentration is present as F^- (aq) ion.

The smaller the K_{sp} value, the lower the solubility of the salt. It follows that the K_{sp} value of a salt can be calculated by determining the solubility of each ion and then using equation 2.10.

2.4.3 CALCULATING THE MOLAR SOLUBILITY FROM K_{SP}

The molar solubility of any slightly soluble salt, along with the concentration of any of its ions, can be calculated from its K_{sp} value. The formula of the salt must be known, however, so that its dissociation and ionization can be written (See Table 2.2).

It is important to note that simply comparing the K_{sp} values of two salts to determine which has a higher or lower molar solubility can often be misleading. This comparison of numerical values is valid only when the two salts have the same stoichiometry, that is, the subscripts in the formulas are identical.

Table 2.2. The solubility product constants of common insoluble salts at 25°C

Salt	Solubility Equilibrium	K_{sp}
Fluorides		
MgF_2	$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$	6.6×10^{-9}
CaF_2	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$	3.9×10^{-11}
SrF_2	$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$	2.9×10^{-9}
BaF_2	$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$	1.7×10^{-6}
LiF	$LiF(s) \rightleftharpoons Li^+(aq) + F^-(aq)$	1.7×10^{-3}
PbF_2	$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$	3.6×10^{-8}
Chlorides		
$CuCl$	$CuCl(s) \rightleftharpoons Cu^+(aq) + Cl^-(aq)$	1.9×10^{-7}
$AgCl$	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	1.8×10^{-10}
Hg_2Cl_2	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$	1.2×10^{-18}
$TlCl$	$TlCl(s) \rightleftharpoons Tl^+(aq) + Cl^-(aq)$	1.8×10^{-4}
$PbCl_2$	$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$	1.7×10^{-5}
$AuCl_3$	$AuCl_3(s) \rightleftharpoons Au^{3+}(aq) + 3Cl^-(aq)$	3.2×10^{-25}
Bromides		
$CuBr$	$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$	5×10^{-9}
$AgBr$	$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$	5.0×10^{-13}
Hg_2Br_2	$Hg_2^{2+}(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Br^-(aq)$	5.6×10^{-23}
$HgBr_2$	$HgBr_2(s) \rightleftharpoons Hg^{2+}(aq) + 2Br^-(aq)$	1.3×10^{-19}
$PbBr_2$	$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$	2.1×10^{-6}
Iodides		
Cul	$Cul(s) \rightleftharpoons Cu^+(aq) + I^-(aq)$	1×10^{-12}
Agl	$Agl(s) \rightleftharpoons Ag^+(aq) + 1^-(aq)$	8.3×10^{-17}
Hg_2l_2	$Hg_2l_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2l^-(aq)$	4.7×10^{-28}
Hgl_2	$Hgl_2(s) \rightleftharpoons Hg^{2+}(aq) + 2l^-(aq)$	1.1×10^{-28}
Pbl_2	$Pbl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2l^-(aq)$	7.9×10^{-9}

(*Continued*)

Salt	Solubility Equilibrium	K_{sp}
Hydroxides		
$Mg(OH)_2$	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$	7.1×10^{-12}
$Ca(OH)_2$	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$	6.5×10^{-6}
$Mn(OH)_2$	$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2OH^-(aq)$	1.6×10^{-13}
$Fe(OH)_2$	$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$	7.9×10^{-16}
$Fe(OH)_3$	$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$	1.6×10^{-39}
$Co(OH)_2$	$Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2OH^-(aq)$	1×10^{-15}
$Co(OH)_3$	$Co(OH)_3(s) \rightleftharpoons Co^{3+}(aq) + 3OH^-(aq)$	3×10^{-45}
$Ni(OH)_2$	$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$	6×10^{-16}
$Cu(OH)_2$	$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$	4.8×10^{-20}
$V(OH)_3$	$V(OH)_3(s) \rightleftharpoons V^{3+}(aq) + 3OH^-(aq)$	4×10^{-35}
$Cr(OH)_3$	$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3OH^-(aq)$	2×10^{-30}
Ag_2O	$Ag_2O(s) + H_2O \rightleftharpoons 2Ag^+(aq) + 2OH^-(aq)$	1.9×10^{-8}
$Zn(OH)_2$	$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$	3.0×10^{-16}
$Cd(OH)_2$	$Cd(OH)_2(s) \rightleftharpoons Cd^{2+}(aq) + 2OH^-(aq)$	5.0×10^{-15}
$Al(OH)_3$ (alpha form)	$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$	3×10^{-34}
Cyanides		
$AgCN$	$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$	2.2×10^{-16}
$Zn(CN)_2$	$Zn(CN)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2CN^-(aq)$	3×10^{-16}
Sulfites		
$CaSO_3$	$CaSO_3(s) \rightleftharpoons Ca^{2+}(aq) + SO_3^{2-}(aq)$	3×10^{-7}
Ag_2SO_3	$Ag^2SO_3(s) \rightleftharpoons 2Ag^+(aq) + SO_3^{2-}(aq)$	1.5×10^{-14}
$BaSO_3$	$BaSO_3(s) \rightleftharpoons Ba^{2+}(aq) + SO_3^{2-}(aq)$	8×10^{-7}
Sulfates		
$CaSO_4$	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$	2.4×10^{-5}
$SrSO_4$	$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$	3.2×10^{-7}

(*Continued*)

Salt	Solubility Equilibrium	K_{sp}
$BaSO_4$	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	1.1×10^{-10}
$RaSO_4$	$RaSO_4(s) \rightleftharpoons Ra^{2+}(aq) + SO_4^{2-}(aq)$	4.3×10^{-11}
Ag_2SO_4	$Ag_2SO_4(s) \rightleftharpoons 2Ag^{+}(aq) + SO_4^{2-}(aq)$	1.5×10^{-5}
Hg_2SO_4	$Hg_2SO_4(s) \rightleftharpoons Hg_2^{2+}(aq) + SO_4^{2-}(aq)$	7.4×10^{-7}
$PbSO_4$	$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$	1.6×10^{-8}
Chromates		
$BaCrO_4$	$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$	2.1×10^{-10}
$CuCrO_4$	$CuCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$	3.6×10^{-6}
Ag_2CrO_4	$Ag_2CrO_4(s) \rightleftharpoons 2Ag^{+}(aq) + CrO_4^{2-}(aq)$	1.2×10^{-12}
Hg_2CrO_4	$Hg_2CrO_4(s) \rightleftharpoons Hg_2^{2+}(aq) + CrO_4^{2-}(aq)$	2.0×10^{-9}
$CaCrO_4$	$CaCrO_4(s) \rightleftharpoons Ca^{2+}(aq) + CrO_4^{2-}(aq)$	7.1×10^{-4}
$PbCrO_4$	$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$	1.8×10^{-14}
Carbonates		
$MgCO_3$	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	3.5×10^{-8}
$CaCO_3$	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	4.5×10^{-9}
$SrCO_3$	$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$	9.3×10^{-10}
$BaCO_3$	$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$	5.0×10^{-9}
$MnCO_3$	$MnCO_3(s) \rightleftharpoons Mn^{2+}(aq) + CO_3^{2-}(aq)$	5.0×10^{-10}
$FeCO_3$	$FeCO_3(s) \rightleftharpoons Fe^{2+}(aq) + CO_3^{2-}(aq)$	2.1×10^{-11}
$CoCO_3$	$CoCO_3(s) \rightleftharpoons Co^{2+}(aq) + CO_3^{2-}(aq)$	1.0×10^{-10}
$NiCO_3$	$NiCO_3(s) \rightleftharpoons Ni^{2+}(aq) + CO_3^{2-}(aq)$	1.3×10^{-7}
$CuCO_3$	$CuCO_3(s) \rightleftharpoons Cu^{2+}(aq) + CO_3^{2-}(aq)$	2.3×10^{-10}
Ag_2CO_3	$Ag_2CO_3(s) \rightleftharpoons 2Ag^{+}(aq) + CO_3^{2-}(aq)$	8.1×10^{-12}
Hg_2CO_3	$Hg_2CO_3(s) \rightleftharpoons 2Hg^{+}(aq) + CO_3^{2-}(aq)$	8.9×10^{-17}
$ZnCO_3$	$ZnCO_3(s) \rightleftharpoons Zn^{2+}(aq) + CO_3^{2-}(aq)$	1.0×10^{-10}
$CdCO_3$	$CdCO_3(s) \rightleftharpoons Cd^{2+}(aq) + CO_3^{2-}(aq)$	1.8×10^{-14}
$PbCO_3$	$PbCO_3(s) \rightleftharpoons Pb^{2+}(aq) + CO_3^{2-}(aq)$	7.4×10^{-14}

(*Continued*)

Salt	**Solubility Equilibrium**	**K_{sp}**
Phosphates		
$Mg_3(PO_4)_2$	$Mg_3(PO_4)_2(s) \rightleftharpoons 3Mg^{2+}(aq) + 2PO_4^{3-}(aq)$	6.3×10^{-26}
$SrHPO_4$	$SrHPO_4(s) \rightleftharpoons Sr^{2+}(aq) + HPO_4^{2-}(aq)$	1.2×10^{-7}
$BaHPO_4$	$BaHPO_4(s) \rightleftharpoons Ba^{2+}(aq) + HPO_4^{2-}(aq)$	4.0×10^{-8}
$LaPO_4$	$LaPO_4(s) \rightleftharpoons La^{3+}(aq) + PO_4^{3-}(aq)$	3.7×10^{-23}
$Fe_3(PO_4)_2$	$Fe_3(PO_4)_2(s) \rightleftharpoons 3Fe^{2+}(aq) + 2PO_4^{3-}(aq)$	1×10^{-36}
Ag_3PO_4	$Ag_3PO_4(s) \rightleftharpoons 3Ag^{+}(aq) + PO_4^{3-}(aq)$	2.8×10^{-18}
$FePO_4$	$FePO_4(s) \rightleftharpoons Fe^{3+}(aq) + PO_4^{3-}(aq)$	4.0×10^{-27}
$Zn_3(PO_4)_2$	$Zn_3(PO_4)_2(s) \rightleftharpoons 3Zn^{2+}(aq) + 2PO_4^{3-}(aq)$	5×10^{-36}
$Pb_3(PO_4)_2$	$Pb_3(PO_4)_2(s) \rightleftharpoons 3Pb^{2+}(aq) + 2PO_4^{3-}(aq)$	3.0×10^{-44}
$Ba_3(PO_4)_2$	$Ba_3(PO_4)_2(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{3-}(aq)$	5.8×10^{-38}
Ferrocyanides		
$Zn_2[Fe(CN)_6]$	$Zn_2[Fe(CN)_6](s) \rightleftharpoons 2Zn^{2+}(aq) + Fe(CN)_6^{4-}(aq)$	2.1×10^{-16}
$Cd_2[Fe(CN)_6]$	$Cd_2[Fe(CN)_6](s) \rightleftharpoons 2Cd^{2+}(aq) + Fe(CN)_6^{4-}(aq)$	4.2×10^{-18}
$Pb_2[Fe(CN)_6]$	$Pb_2[Fe(CN)_6](s) \rightleftharpoons 2Pb^{2+}(aq) + Fe(CN)_6^{4-}(aq)$	9.5×10^{-19}

Example 2.10

Calculate

A. The molar solubility of calcium fluoride, CaF_2, and
B. The concentration of the fluoride ion, in solution at 25°C. The K_{sp} of CaF_2 is 4.0×10^{-11} at 25°C. Here, the unit of K_{sp} is $(moles/L)^3$ or M^3. This unit may change depending on the identity, that is, the subscripts of the ions, of the salt.

Solution

A. The equilibrium for the salt is as follows:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

The K_{sp} expression is:

$$K_{sp} = [Ca^{2+}][F^-]^2 = 4.0 \times 10^{-11} M^3$$

Let S = the solubility (saturation concentration) of the Ca^{2+} ion in moles per liter.
Then $2S$ = the solubility (saturation concentration) of the F^- ion.
Substitute S into the K_{sp} expression:

$$(S)(2S)^2 = 4.0\times10^{-11}$$

$$4S^3 = 4.0\times10^{-11}$$

$$S = 2.15\times10^{-4}\ M$$

Thus, the molar solubility of a CaF_2 is 2.15×10^{-4} M. This is also $[Ca^{2+}]$.

B. $[F^-] = 2 \times 2.15 \times 10^{-4} M = 4.30 \times 10^{-4} M$

Example 2.11

The molar solubility of tin iodide, SnI_2, is 1.28×10^{-2} mol/L. What is K_{sp} for this compound?

Solution

The solubility equilibrium for SnI_2 is:

$$SnI_2(s) \rightleftharpoons Sn^{2+}(aq) + 2I^-(aq)$$

The K_{sp} expression is

$$K_{sp} = [Sn^{2+}][I^-]^2$$

Note that 1.0 mol of SnI_2 produces 1.0 mol of Sn^{2+}, but 2.0 mol of I^-.

$$[Sn^{2+}] = 1.28 \times 10^{-2}\ M$$

$$[I^-] = (2) \times 1.28 \times 10^{-2}\ M = 2.56 \times 10^{-2}\ M$$

Substituting these values into the K_{sp} expression yields:

$$K_{sp} = (1.28 \times 10^{-2}\ M)(2.56 \times 10^{-2}\ M)^2 = 8.4 \times 10^{-6}\ M^3$$

2.4.4 COMMON AND UNCOMMON ION, AND PH EFFECTS

Occasionally, the solvent in which a salt is to be dissolved is not pure water but rather contains an ion in common with the salt to be dissolved. The common ion may be a cation or an anion, such as Ca^{2+} or F^-. The common ion may also be the H^+ ion or OH^- ion, which manifests itself in a pH value less than or greater than 7, respectively. This is the **common ion effect**, and the net result is to reduce significantly the solubility of the salt in question.

The presence of a background salt with no ions in common with the salt to be dissolved is known as the **uncommon ion** or **salt effect**. In contrast, this effect only slightly increases the solubility of the salt in question.

In general, most salts are more soluble in hot water than in cold; that is, the solubility of most salts increase with increasing temperature. In the temperature range of 0°C to 100°C, many common salts demonstrate a nearly linear relationship between solubility and temperature, with varying, positive slopes. Some notable exceptions include KNO_3, which shows an exponential relationship, and Li_2SO_4, which shows a linear but decreasing solubility with temperature.

Example 2.16

Magnesium hydroxide, $Mg(OH)_2$, is a common antacid and has a $K_{sp} = 1.8 \times 10^{-11}\ M^3$. Its limited solubility is what makes this otherwise strong base suitable as an antacid for human consumption. Find the molar solubility of $Mg(OH)_2$ in a laboratory solution whose pH is 13.12.

Solution

To find the molar solubility of $Mg(OH)_2$ in distilled water, the method outlined in Example 2.10 would be followed. In this case, however, the solution is basic with an excess of OH^- ions. Since these OH^- ions are in common with the OH^- ions contained in $Mg(OH)_2$, the common ion effect must be taken into account because it will reduce the solubility of $Mg(OH)_2$.

First determine $[OH^-]$ as follows:

$$pOH = 14.00 - pH = 14.00 - 13.12 = 0.88$$

$$[OH^-] = 10^{-pOH} = 10^{-0.88} = 1.32 \times 10^{-1}\ M$$

The K_{sp} expression for $Mg(OH)_2$ is:

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

Use the strategy outlined in Example 2.10.

Let $[Mg^{2+}] = S$
And $[OH^-] = 2S + 1.32 \times 10^{-1}$

This is true because the *total* hydroxide ion concentration is the sum of the contribution of hydroxide ion coming from the already alkaline solution, that is, 1.32×10^{-1} M, *plus* the contribution of hydroxide ion coming from the $Mg(OH)_2$ source, represented as 2S, since the hydroxide ion concentration must be twice the magnesium ion concentration, as indicated in the chemical formula of $Mg(OH)_2$.

Now substitute these values, along with K_{sp} value, in the K_{sp} expression:

$$1.8 \times 10^{-11} = (S)(2S + 1.32 \times 10^{-1})^2$$

This is a cubic equation in *S*. To simplify the calculation, assume that 2*S* term is negligible compared with 1.32×10^{-1} as an additive term. Then:

$$1.8 \times 10^{-11} = (S)(1.32 \times 10^{-1})^2$$

$$S = 1.0 \times 10^{-9}\ M$$

This result represents the molar solubility of $Mg(OH)_2$.

2.4.5 PREDICTING PRECIPITATION

When two solutions are mixed, it is possible that an insoluble precipitate will form and settle to the bottom. Whether this happens depends on the identities of the ions present in the solutions and their respective concentrations. If the ions for a potentially insoluble precipitate are present, all that needs to be done to predict precipitation is to calculate a hypothetical solubility product constant, *Q,* in the same manner as K_{sp} is calculated. The *Q* value is then compared to the K_{sp} value, subject to the following criteria or conditions:

- If $Q \leq K_{sp}$, no precipitate forms.
- If $Q > K_{sp}$, a precipitate forms.

In general, conditions that favor **completeness of precipitation** are as follows:

- A very small value of K_{sp}
- High initial ion concentrations
- A concentration of common ion that considerably exceeds the concentration of the target ion to be precipitated

Example 2.17

Will a precipitate form if 50.0 mL of 1.2×10^{-3} M $Pb(NO_3)_2$ is added to 50.0 mL of 2.0×10^{-4} M Na_2SO_4?

Solution

The addition of the two solutions will result in a double-replacement reaction. Two products $NaNO_3$ and $PbSO_4$ will form and are thus candidates of insoluble salts. A check of Table 2.2 reveals that only $PbSO_4$ has a K_{sp} value (1.6×10^{-8}) and is therefore a possible precipitate. To confirm whether a precipitate actually forms, evaluate *Q* as follows:

$$Q = [Pb^{2+}(aq)][SO_4^{2-}(aq)]$$

$$[Pb^{2+}(aq)] = \frac{(0.050\ L)(1.2\times10^{-3}\ M)}{0.100\ L}$$
$$= 6.0\times10^{-4}\ M$$

$$[SO_4^{2-}(aq)] = \frac{(0.050\ L)(2.0\times10^{-4}\ M)}{0.100\ L}$$
$$= 1.0\times10^{-4}\ M$$

Substitute these values for concentrations into the expression for *Q*:

$$Q = (6.0\times10^{-4}\ M)(1.0\times10^{-4}\ M)$$
$$= 6.0\times10^{-8}\ M$$

But $K_{sp} = 1.6 \times 10^{-8}$

Since $Q > K_{sp}$, then a precipitate forms!

2.5 COMPLEX ION FORMATION

2.5.1 BASIC CONCEPT

A **complex ion** consists most commonly of a metal atom or ion, such as Co^{3+}, and attached groups called *ligands*. Ligands may be neutral molecules, such as NH_3, or anions, such as Cl^-. Furthermore, the ligands may be of all one type, as in $[Co(NH_3)_6]^{3+}$ or of different types, as in $[CoCl(NH_3)_5]^{2+}$.

The region surrounding the central atom or ion and its ligands is called the *coordination sphere*. The coordination number is the total number of points at which the central atom or ion attaches to its ligands. Both $[Co(NH_3)_6]^{3+}$ and $[CoCl(NH_3)_5]^{2+}$ have coordination numbers of 6. The most common coordination numbers observed in complex ions are 2, 4, and 6. If the complex carries a net electric charge, as the two examples given here do, it is called a **complex ion**. If it is electrically neutral, it is referred to as a coordination compound. An example of a coordination compound is $[Co(NH_3)_6]Cl_3$.

Many complex ions are colored because the energy differences in the *d* orbitals match the components of visible light. Substituting one ligand for another produces subtle changes in the energy levels of the *d* orbitals and striking changes in the colors of complex ions. For example, a solution of $[Cr(H_2O)_6]^{3+}$ is violet, while a solution of $[Cr(NH_3)_6]^{3+}$ is yellow.

2.5.2 CHELATING AND SEQUESTERING AGENTS

EDTA is short for ethylenediaminetetraacetic acid. When it acts as a ligand in water, it exists as the ethylenediaminetetraacetate anion $[EDTA]^{4-}$. This anion has a remarkable ability to form complex ions with metal cations in water which are significantly more stable than ordinary complex ions. It is referred to as a **chelating agent** and its complex ions are called chelates.

$[EDTA]^{4-}$ will form chelates with hard water ions such Fe^{2+}, Mg^{2+}, and Ca^{2+}. See Figure 2.1. When it is added to boiler water, it removes these hard water metal ions so effectively that it is referred to as a **sequestering**

agent. It actually stops boiler scale buildup. Chelation with $[EDTA]^{4-}$ also prevents the growth of certain bacteria in liquid soaps and shampoos. By sequestering Ca^{2+} and Mg^{2+} ions, which are important constituents of bacterial cell walls, the cell walls disintegrate and the bacteria die.

The original EDTA molecule shown in Figure 2.1 (A) has been contorted to show its coordination sphere and bonding with Ca^{2+} illustrated as dashed lines shown in B. The complex has a net charge of +2.

EDTA may be administered in chelation therapy to remove heavy metals, such as lead or cadmium, from humans who have been exposed to these toxins.

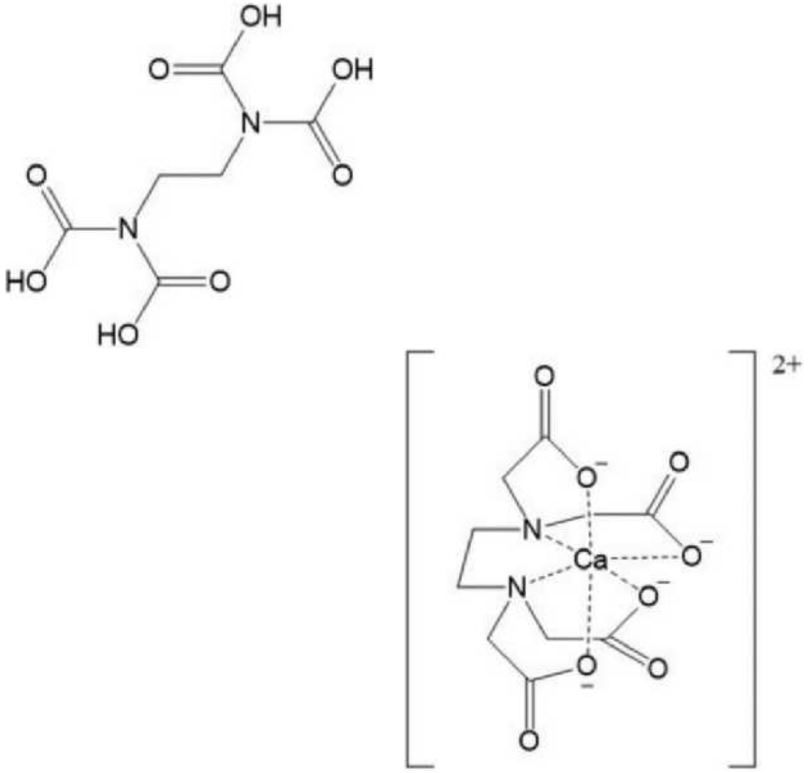

Figure 2.1. The molecular structure of (A) EDTA and (B) EDTA complex of calcium ion

2.6 CHEMICAL KINETICS

2.6.1 BASIC CONCEPT

Chemical kinetics is the study of the rates and mechanisms of chemical reactions. The reaction rate is a kinetic property and depends on the mechanism. In contrast, thermodynamic properties (discussed in Section 2.7) are independent of mechanism. Thermodynamics indicates whether or not a reaction is spontaneous, but kinetics indicates how fast the reaction occurs, and whether it happens fast enough to be of any interest or value.

The easiest way to measure the rate of reactions is by measuring the disappearance of a reactant, that is, the change in concentration of a reactant with time. Thus,

$$\text{Reaction rate} = \frac{-\Delta C}{\Delta t} = \frac{-(C_2 - C_1)}{t_2 - t_1}$$

where ΔC = the change in the concentration of the reactant and Δt = the elapsed time. The subscripts 1 and 2 refer to concentrations and corresponding times, respectively. The reactant concentration decreases with time, making $(C_2 - C_1)$ a negative quantity. The minus sign is used to make it a positive quantity.

The reaction rate can be calculated just as well from the change in concentration with time of a product, in which case $\Delta C/\Delta t$ is a positive quantity. It is important to remember that the reaction rate is constantly changing, so $\Delta C/\Delta t$ represents an average rate. The instantaneous rate is given by the first derivative $\mathrm{d}C/\mathrm{d}t$.

2.6.2 REACTION RATE LAWS, ORDERS, AND CONSTANTS

For the general reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow g\mathrm{G} + h\mathrm{H}$$

the **rate law** or **rate equation** is expressed as

$$\text{Rate} = \mathrm{k}[\mathrm{A}]^x[\mathrm{B}]^y \tag{2.12}$$

where k = the **rate constant** (in reciprocal time and concentration units), [A] and [B] represent the molar concentrations of reactants A and B, and x

and *y* are exponents denoting the **order** of the reaction for the reactant species. The exponents *x* and *y* must be determined experimentally. The sum of the exponents (*x* + *y*) is called the **overall order** of the reaction. In the present case, it is said that the reaction is *x* order in A, *y* order in B, and (*x* + *y*) order overall.

Consider, for example, the following reaction:

$$NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g) \tag{2.13}$$

Experimentally, it is determined that the rate law for this reaction is

$$\text{Rate} = k[NO_2]^2 \tag{2.14}$$

This means that the rates are second order in NO_2, zeroth order in CO_2, and second order overall.

Consider, as another example, the decomposition of dinitrogen pentoxide, N_2O_5:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g) \tag{2.15}$$

Here, it is experimentally determined that the rate law for this reaction is

$$\text{Rate} = k[N_2O_5] \tag{2.16}$$

Thus, the rate of decomposition is first order in N_2O_5. The rate constant k is also experimentally measured:

$$k = 5.2 \times 10^{-3} \text{ at } 65°C$$

2.6.3 FIRST AND SECOND-ORDER REACTIONS

For any reaction that is known to be first order in a particular species, as in the N_2O_5 decomposition discussed earlier, the rate can be written as

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{-\Delta[A]}{\Delta t} = k[A] \tag{2.17}$$

For a **first-order reaction,** this means that doubling the concentration of A doubles the reaction rate. This equation may be integrated to give a more useful result:

$$\text{In}\,\frac{[\text{A}]_0}{[\text{A}]} = \text{k}\Delta t \tag{2.18}$$

This can also be written in a more user-friendly way as:

$$\ln[\text{A}] = \ln[\text{A}]_0 - \text{k}\Delta t \tag{2.19}$$

In similar fashion, the integrated rate equation for a **second-order reaction** is:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + \text{k}\Delta t \tag{2.20}$$

Note that $[\text{A}]_0$ represents the concentration of species A at time zero, which may or may not be the same as the iinitial concentration, while [A] represents its concentration at any time t in the future.

2.6.4 HALF-LIFE OF A REACTION

A quantity defined as the half-life of the reaction can also be determined. The **half-life** is the time required for the concentration of the reactant to reach half of its initial value. For a *first-order reaction,* the half-life is independent of the initial concentration and is given as:

$$t_{1/2} = \frac{0.693}{\text{k}} \tag{2.21}$$

For a second-order reaction, the half-life depends on initial concentration and is given as:

$$t_{1/2} = \frac{1}{\text{k}[\text{A}]_0} \tag{2.22}$$

Example 2.18

Consider the following reaction between peroxydisulfate ion, $S_2O_8^{2-}$, and iodide ion, I^- and the experimental data about the concentrations and reaction rates at 25°C given in Table 2.3.

$$S_2O_8^{2-}(aq) + 3I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$

Table 2.3. Experimental data for the reaction kinetics of peroxydisulfate

Expt. Number	**$[S_2O_8^{2-}$ (aq)]**	**$[I^-$(aq)]**	**Initial Rate**
1	0.080 M	0.034 M	2.2×10^{-4} M/sec
2	0.080 M	0.017 M	1.1×10^{-4} M/sec
3	0.16 M	0.017 M	2.2×10^{-4} M/sec

A. Write the rate law expression and determine the overall order, that is, $(x + y)$, for this reaction.
B. Determine the rate constant k for this reaction at 25°C.

Solution

A. Examine the data given in Table 2.3. Comparing Experiment #1 with #2, it can be seen that doubling the iodide ion concentration while holding the peroxydisulfate ion concentration constant, would double the reaction rate. Similarly, comparing Experiment #2 with #3 reveals that doubling the peroxydisulfate ion concentration while holding the iodide ion concentration constant, would also double the reaction rate.

Thus, this reaction is first order (or linear) in iodide ion concentration, and first order (or linear) in peroxydisulfate ion concentration. The rate law can be written as follows:

$$\text{Rate} = \text{k}[S_2O_8^{2-}]^x[I^-]^y$$

where $x = 1$ and $y = 1$.

Hence,

$$\text{Rate} = \text{k}[S_2O_8^{2-}]^1[I^-]^1$$

The overall order is $(x + y) = (1 + 1) = 2$, indicating second order overall.

B. The rate constant k can be determined using the data from any of the three experiments. Take the data from Experiment #1, and use the rate law expression determined in **A.** Thus,

$$2.2\times10^{-4}\ \text{M/sec} = \text{k}(0.034\ \text{M})^1(0.080\ \text{M})^1$$

$$\text{k} = 8.09\times10^{-2}(\text{M}\times\text{sec})^{-1}$$

Example 2.19

The thermal decomposition of phosphine, PH_3, is known to be a first-order reaction:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

The half-life, $t_{1/2}$, is 35.0 sec at 680°C.

A. Compute the rate constant k for this reaction.
B. Find the time required for 75% of the initial concentration of PH_3 to decompose.

Solution

A. For a first-order reaction, $t_{1/2} = 0.693/\mathrm{k}$.

Hence,

$$\mathrm{k} = \frac{0.693}{t_{1/2}} = \frac{0.693}{35.0\ \mathrm{sec}} = 0.0198\ \mathrm{sec}^{-1}$$

B. To find the time, use the integrated, first-order rate law, equation 2.18 or 2.19, and solve for Δt. If 75% of PH_3 is to decompose, 25% must remain! Thus,

$$[\mathrm{A}]_0 = 100\% = 1.00$$
$$[\mathrm{A}] = 25\% = 0.250$$

Either equation 2.18 or 2.19 may be used. First, rearrange equation 2.19 and solve for Δt:

$$k\Delta t = \ln[\mathrm{A}]_0 - \ln[\mathrm{A}]$$

$$\Delta t = \{\ln[\mathrm{A}]_0 - \ln[\mathrm{A}]\}/\mathrm{k}$$

Now substitute these values into equation 2.19 and solve for Δt:

$$\Delta t = \{\ln(1.00) - \ln(0.250)\}/0.0198\ \mathrm{sec}^{-1}$$

$$\Delta t = 70.0\ \mathrm{sec}$$

2.6.5 DEPENDENCE ON TEMPERATURE: THE ARRHENIUS EQUATION

The Arrhenius model for rates of reactions assumes that molecules must undergo collisions before they can react. The number of collisions per unit time is **A,** the **frequency factor.** This model also assumes that not all collisions will result in or lead to a reaction. Rather, only those with sufficient energy, called the **activation energy, E_a (**to allow molecules to reach an **activated complex),** will achieve this result.

The rate constant k is a function of temperature and can be expressed theoretically as the **Arrhenius equation:**

$$\mathrm{k} = \mathrm{A}e^{-E_\mathrm{a}/\mathrm{R}T} \tag{2.23}$$

where

A = the frequency factor, a measure of the number of collisions per second,

E_a = the activation energy in joules or calories per mole,

R = the universal gas constant in units consistent with those for E_a,

T = the absolute temperature in kelvins.

A more useful form of the equation can be written as:

$$\ln \mathrm{k} = \ln \mathrm{A} - \frac{E_\mathrm{a}}{\mathrm{R}T} \tag{2.24}$$

The rate constants k_1 and k_2 at two different temperatures, T_1 and T_2, respectively, can be written as two separate equations, using equation 2.24. The equations can be divided by each other and the result rearranged such that the rate constants are related as follows:

$$\mathrm{In}\,\frac{\mathrm{k}_1}{\mathrm{k}_2} = \frac{E_\mathrm{a}}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2.25}$$

Example 2.20

The following reaction between nitric oxide and ozone is important in the chemistry of air pollution as discussed in Chapter 2 in Applied Chemistry for Environmental Engineering:

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

The frequency factor $A = 8.70 \times 10^{12}$ sec^{-1} and the rate constant $k = 300$ sec^{-1} at 75°C.

A. Find the activation energy, E_a, in joules per mole for this reaction.
B. Find the rate constant k of this reaction at 0°C, assuming E_a to be constant.

Solution:

A. Use the Arrhenius equation and solve for E_a.

$$\ln k = \ln A - \frac{E_a}{RT}$$

Use $R = 8.31$ J/K × mol and $T = 273 + 75°\text{C} = 348$ K. Then,

$$\ln 300 = \ln 8.70 \times 10^{12} - \frac{E_a}{(8.31)(348)}$$

$E_a = 69{,}700$ J/mol or 69.7 kJ/mol

B. Denote the rate constant given at 75°C as k_1 and the rate constant at 0°C as k_2, and use equation 2.25:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substitute the above information, and solve for k_2.

$$\ln k_2 = \ln 300 - \frac{69{,}700}{8.31}\left(\frac{1}{273} - \frac{1}{348}\right)$$

$$= 5.7038 - 6.6210 = -0.9172$$

$$k_2 = 0.3996 \text{ sec}^{-1} = 0.400 \text{ sec}^{-1}$$

2.6.6 CATALYSIS

Substances that increase the rate of reaction without themselves being consumed in the reaction are called **catalysts**. They work by lowering the activation energy, E_a, or the barrier required for the reaction to proceed. A catalyst may be in the same physical state as the other species in the reaction (homogeneous catalysis) or in a different physical state (heterogeneous catalysis).

2.7 CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

2.7.1 BASIC CONCEPT

Thermodynamics is the study of energy transformations. **Thermochemistry** is the study of the thermal energy changes that accompany chemical and physical changes. **Heat** is one form of energy. Heat is the energy transferred between objects or systems, which may be measured by temperature changes. The total energy is a property of a substance or system; it cannot be measured directly.

Any process occurring within a system that produces or releases heat into the surroundings is called **exothermic**, and its value is given a negative sign by convention. Any process that absorbs heat from the surroundings into the system is called **endothermic**, and its value has a positive sign. Note that an exothermic reaction is not necessarily a spontaneous reaction, and its negative sign should *not* be interpreted as such. This type of interpretation and criterion is reserved for ΔG, the **Gibbs free energy change**, defined in equation 2.34 and discussed thereafter.

2.7.2 ENTHALPY AND HESS'S LAW

Since chemical reactions involve the breaking and making of bonds, energy changes generally accompany reactions. To initiate a reaction, an activation energy, E_a, must first be supplied for the reactants to reach an activated complex, whether or not the reaction is spontaneous. When a reaction occurs, a change in **enthalpy,** that is, heat content, also known as the **heat of reaction**, $\Delta \boldsymbol{H}_{RX}$, occurs. This is the amount of heat exchanged—either liberated or absorbed—with the surroundings under constant external pressure. Recall Figure 1.1 on exothermic and endothermic reactions for clarification. It may be measured experimentally (directly) or calculated theoretically (indirectly), and expressed in either kilojoules (kJ) or kilocalories (kcal).

The enthalpy change, known as the **standard heat of formation,** ΔH_f^o, is defined as the heat of reaction for a product derived only from its elements, the superscript ^{o} meaning measured under standard conditions (usually at STP). See Table 2.4 for thermodynamic values of common substances.

Table 2.4. Thermodynamic constants for the changes of formation in enthalpy, entropy, and Gibbs free energy at STP

Aluminum	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Al (s)	0	0	28.3
$AlCl_3$ (s)	−704.2	−628.8	110.7
Al_2O_3 (s)	−1,675.7	−1,582.3	50.9
$Al(OH)_3$ (s)	−1,277.0		

Barium	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Ba (s)	0	0	67.0
$BaCl_2$ (s)	−858.6	−810.4	123.7
$BaCO_3$ (s)	−1,219.0	−1,139.0	112.0
BaO (s)	−553.5	−525.1	70.4
$Ba(OH)_2$ (s)	−946.0		
$BaSO_4$ (s)	−1,473.2	−1,362.2	132.2

Beryllium	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Be (s)	0	0	9.5
BeO (s)	−599.0	−569.0	14.0
$Be(OH)_2$ (s)	−902.5	−815.0	51.9

Bromine	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Br (g)	111.9	82.4	175.0
Br_2 (l)	0	0	152.2
Br_2 (g)	30.9	3.1	245.5
Br_2 (aq)	−3.0	4.0	130.0
Br^- (aq)	−121.0	−175.0	82.0
BrF_3 (g)	−255.6	−229.4	292.5
HBr (g)	−36.3	−53.5	198.7

(*Continued*)

Cadmium	**ΔH^{o}_{f} (kJ/mol)**	**ΔG^{o}_{f} (kJ/mol)**	**S^{o} (J/mol K)**
Cd (s)	0	0	52.0
CdO (s)	−258.0	−228.0	55.0
$Cd(OH)_2$ (s)	−561.0	−474.0	96.0
CdS (s)	−162.0	−156.0	65.0
$CdSO_4$ (s)	−935.0	−823.0	123.0

Calcium	**ΔH^{o}_{f} (kJ/mol)**	**ΔG^{o}_{f} (kJ/mol)**	**S^{o} (J/mol K)**
Ca (s)	0	0	41.4
Ca (g)	178.2	144.3	158.9
Ca^{2+} (g)	1,925.9		
CaC_2 (s)	−59.8	−64.9	70.0
$CaCO_3$ (s, calcite)	−1,206.9	−1,128.8	92.9
$CaCl_2$ (s)	−795.8	−748.1	104.6
CaF_2 (s)	−1,219.6	−1,167.3	68.9
CaH_2 (s)	−186.2	−147.2	42.0
CaO (s)	−635.1	−604.0	39.8
CaS (s)	−482.4	−477.4	56.5
$Ca(OH)_2$ (s)	−986.1	−898.5	83.4
$Ca(OH)_2$ (aq)	−1,002.8	−868.1	−74.5
$Ca_3(PO_4)_2$ (s)	−4,126.0	−3,890.0	241.0
$CaSO_4$ (s)	−1,434.1	−1,321.8	106.7
$CaSiO_3$ (s)	−1,630.0	−1,550.0	84.0

Carbon	**ΔH^{o}_{f} (kJ/mol)**	**ΔG^{o}_{f} (kJ/mol)**	**S^{o} (J/mol K)**
C (s, graphite)	0	0	5.7
C (s, diamond)	1.9	2.9	2.4

(*Continued*)

Carbon	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
C (g)	716.7	671.3	158.1
CCl_4 (l)	−135.4	−65.2	216.4
CCl_4 (g)	−102.9	−60.6	309.9
$CHCl_3$ (l)	−134.5	−73.7	201.7
$CHCl_3$ (g)	−103.1	−70.3	295.7
CH_4 (g)	−74.8	−50.7	186.3
CH_3OH (g)	−200.7	−162.0	239.8
CH_3OH (l)	−238.7	−166.3	126.8
H_2CO (g)	−116.0	−110.0	219.0
HCOOH (g)	−363.0	−351.0	249.0
HCN (g)	135.1	125.0	202.0
C_2H_2 (g)	226.7	209.2	200.9
C_2H_4 (g)	52.3	68.2	219.6
CH_3CHO (g, acetaldehyde)	−166.0	−129.0	250.0
C_2H_4O (g, ethylene oxide)	−53.0	−13.0	242.0
CH_3CH_2OH (l)	−277.7	−174.8	160.7
CH_3CH_2OH (g)	−235.1	−168.5	282.7
CH_3COOH (l)	−484.0	−389.0	160.0
C_2H_6 (g)	−84.7	−32.8	229.6
C_3H_6 (g)	20.9	62.7	266.9
C_3H_8 (g)	−103.8	−23.5	269.9
$CH_2{=}CHCN$ (l)	152.0	190.0	274.0
C_6H_6 (l)	49.0	124.5	172.8
$C_6H_{12}O_6$ (s)	−1,275.0	−911.0	212.0
CO (g)	−110.5	−137.2	197.7

(*Continued*)

Carbon	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
CO_2 (g)	−393.5	−394.4	213.7
CS_2 (g)	117.4	67.1	237.8
$COCl_2$ (g)	−218.8	−204.6	283.5

Chlorine	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Cl (g)	121.7	105.7	165.2
Cl_2 (g)	0	0	223.1
Cl_2 (aq)	−23.0	7.0	121.0
Cl^- (aq)	−167.0	−131.0	57.0
Cl^- (g)	−233.1		
HCl (g)	−92.3	−95.3	186.9
HCl (aq)	−167.2	−131.2	56.5

Chromium	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Cr (s)	0	0	23.8
Cr_2O_3 (s)	−1,139.7	−1,058.1	81.2
CrO_3 (s)	−579.0	−502.0	72.0
$CrCl_3$ (s)	−556.5	−486.1	123.0

Copper	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Cu (s)	0	0	33.2
$CuCl_2$ (s)	−220.1	−175.7	108.1
$CuCO_3$ (s)	−595.0	−518.0	88.0
Cu_2O (s)	−170.0	−148.0	93.0
CuO (s)	−157.3	−129.7	42.6
$Cu(OH)_2$ (s)	−450.0	−372.0	108.0
CuS (s)	−49.0	−49.0	67.0

(*Continued*)

Fluorine	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
F_2 (g)	0	0	202.8
F (g)	79.0	61.9	158.8
F^- (g)	−255.4		
F^- (aq)	−332.6	−278.8	−13.8
HF (g)	−271.1	−273.2	173.8
HF (aq)	−332.6	−278.8	88.7

Hydrogen	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
H_2 (g)	0	0	130.7
H (g)	218.0	203.2	114.7
H^+ (g)	1,536.2		
H^+ (aq)	0		
OH^- (aq)	−230.0	−157.0	−11.0
H_2O (l)	−285.8	−237.1	69.9
H_2O (g)	−241.8	−228.6	188.8
H_2O_2 (l)	−187.8	−120.4	109.6

Iodine	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
I_2 (s)	0	0	116.1
I_2 (g)	62.4	19.3	260.7
I_2 (aq)	23.0	16.0	137
I (g)	106.8	70.3	180.8
I^- (g)	−197.0		
I^- (aq)	−55.0	−52.0	106.0
ICl (g)	17.8	−5.5	247.6

(*Continued*)

Iron	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Fe (s)	0	0	27.8
Fe_3C (s)	21.0	15.0	108.0
$FeCl_2$ (s)	−341.8	−302.3	118.0
$FeCl_3$ (s)	−399.5	−333.9	142.3
$Fe_{0.95}O$ (s) (wustite)	−264.0	−240.0	59.0
FeO (s)	−272.0		
Fe_3O_4 (s, magnetite)	−1,118.4	−1,015.4	146.4
Fe_2O_3 (s, hematite)	−824.2	−742.2	87.4
FeS (s)	−95.0	−97.0	67.0
FeS_2 (s, pyrite)	−178.2	−166.9	52.9
$FeSO_4$ (s)	−929.0	−825.0	121.0
$Fe(CO)_5$ (l)	−774.0	−705.3	338.1

Lead	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Pb (s)	0	0	64.8
$PbCl_2$ (s)	−359.4	−314.1	136.0
PbO (s, yellow)	−217.3	−187.9	68.7
PbO_2 (s)	−277.0	−217.0	69.0
PbS (s)	−100.4	−98.7	91.2
$PbSO_4$ (s)	−920.0	−813.0	149.0

Magnesium	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Mg (s)	0	0	32.7
$MgCl_2$ (s)	−641.3	−591.8	89.6
$MgCO_3$ (s)	−1,095.8	−1,012.1	65.7
MgO (s)	−601.7	−569.4	26.9

(*Continued*)

Magnesium	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
$Mg(OH)_2$ (s)	−924.5	−833.5	63.2
MgS (s)	−346.0	−341.8	50.3

Manganese	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Mn (s)	0	0	32.0
MnO (s)	−385.0	−363.0	60.0
Mn_3O_4 (s)	−1,387.0	−1,280.0	149.0
Mn_2O_3 (s)	−971.0	−893.0	110.0
MnO_2 (s)	−521.0	−466.0	53.0
MnO_4^- (aq)	−543.0	−449.0	190.0

Mercury	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Hg (l)	0	0	75.9
$HgCl_2$ (s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.7
HgO (s, red)	−90.8	−58.5	70.3
HgS (s, red)	−58.2	−50.6	82.4

Nickel	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
Ni (s)	0	0	29.9
$NiCl_2$ (s)	−305.3	−259.0	97.7
NiO (s)	−239.7	−211.7	38.0
$Ni(OH)_2$ (s)	−538.0	−453.0	79.0
NiS (s)	−93.0	−90.0	53.0

(*Continued*)

Nitrogen	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
N_2 (g)	0	0	191.6
N (g)	472.7	455.6	153.3
NH_3 (g)	−46.1	−16.5	192.5
NH_3 (aq)	−80.0	−27.0	111.0
NH_4^+ (aq)	−132.0	−79.0	113.0
NO (g)	90.3	86.6	210.8
NOCl (g)	51.7	66.1	261.8
NO_2 (g)	33.9	51.3	240.1
N_2O (g)	82.1	104.2	219.9
N_2O_4 (g)	9.2	97.9	304.3
N_2O_4 (l)	−19.5	97.0	209.0
N_2O_5 (s)	−42.0	134.0	178.0
N_2H_4 (l)	50.6	149.3	121.2
$N_2H_3CH_3$ (l)	54.0	180.0	166.0
HNO_3 (aq)	−207.4	−111.3	146.4
HNO_3 (l)	−174.1	−80.7	155.6
HNO_3 (g)	−135.1	−74.7	266.4
NH_4ClO_4 (s)	−295.0	−89.0	186.0
NH_4Cl (s)	−314.4	−202.9	94.6
NH_4Cl (aq)	−299.7	−210.5	169.9
NH_4NO_3 (s)	−365.6	−183.9	151.1
NH_4NO_3 (aq)	−339.9	−190.6	259.8

Oxygen	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
O_2 (g)	0	0	205.1
O (g)	249.2	231.7	161.1
O_3 (g)	142.7	163.2	238.9

(*Continued*)

Phosphorus	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
P (s, white)	0	0	164.4
P (s, red)	−70.4	−48.4	91.2
P (s, black)	−39.0	−33.0	23.0
P (g)	314.6	278.3	163.2
P_4 (s, white)	0	0	41.1
P_4 (s, red)	−17.6	−12.1	22.8
P_4 (g)	59.0	24.0	280.0
PF_5 (g)	−1,578.0	−1,509.0	296.0
PH_3 (g)	5.4	13.4	210.2
PCl_3 (g)	−287.0	−267.8	311.8
H_3PO_4 (l)	−1,279.0	−1,119.1	110.5
H_3PO_4 (aq)	−1,288.0	−1,143.0	158.0
P_4O_{10} (s)	−2,984.0	−2,697.7	228.9

Potassium	**ΔH^o_f (kJ/mol)**	**ΔG^o_f (kJ/mol)**	**S^o (J/mol K)**
K (s)	0	0	64.2
KCl (s)	−436.7	−409.1	82.6
$KClO_3$ (s)	−397.7	−296.3	143.1
$KClO_4$ (s)	−433.0	−304.0	151.0
KI (s)	−327.9	−324.9	106.3
K_2O (s)	−361.0	−322.0	98.0
K_2O_2 (s)	−496.0	−430.0	113.0
KO_2 (s)	−283.0	−238.0	117.0
KOH (s)	−424.8	−379.1	78.9
KOH (aq)	−482.4	−440.5	91.6

(*Continued*)

Silicon	**ΔH^{o}_{f} (kJ/mol)**	**ΔG^{o}_{f} (kJ/mol)**	**S^{o} (J/mol K)**
Si (s)	0	0	18.3
$SiBr_4$ (l)	−457.3	−443.9	277.8
SiC (s)	−65.3	−62.8	16.6
$SiCl_4$ (g)	−657.0	−617.0	330.7
SiH_4 (g)	34.3	56.9	204.6
SiF_4 (g)	−1,614.9	−1,572.7	282.5
SiO_2 (s, quartz)	−910.9	−856.6	41.8

Silver	**ΔH^{o}_{f} (kJ/mol)**	**ΔG^{o}_{f} (kJ/mol)**	**S^{o} (J/mol K)**
Ag (s)	0	0	42.6
Ag^+ (aq)	105.0	77.0	73.0
AgBr (s)	−100.0	−97.0	107.0
AgCN (s)	146.0	164.0	84.0
AgCl (s)	−127.1	−109.8	96.2
Ag_2CrO_4 (s)	−712.0	−622.0	217.0
AgI (s)	−62.0	−66.0	115.0
Ag_2O (s)	−31.1	−11.2	121.3
$AgNO_3$ (s)	−124.4	−33.4	140.9
Ag_2S (s)	−32.0	−40.0	146.0

Sodium	**ΔH^{o}_{f} (kJ/mol)**	**ΔG^{o}_{f} (kJ/mol)**	**S^{o} (J/mol K)**
Na (s)	0	0	51.2
Na (g)	107.3	76.8	153.7
Na^+ (g)	609.4		
Na^+ (aq)	−240.0	−262.0	59.0
NaBr (s)	−361.0	−349.0	86.8

(*Continued*)

Sodium	**ΔH°_f (kJ/mol)**	**ΔG°_f (kJ/mol)**	**S° (J/mol K)**
Na_2CO_3 (s)	−1,130.7	−1,044.4	135.0
$NaHCO_3$ (s)	−948.0	−852.0	102.0
NaCl (s)	−411.2	−384.1	72.1
NaCl (g)	−176.7	−196.7	229.8
NaCl (aq)	−407.3	−393.1	115.5
NaH (s)	−56.0	−33.0	40.0
NaI (s)	−288.0	−282.0	91.0
$NaNO_2$ (s)	−359.0		
$NaNO_3$ (s)	−467.0	−366.0	116.0
Na_2O (s)	−416.0	−377.0	73.0
Na_2O_2 (s)	−515.0	−451.0	95.0
NaOH (s)	−425.6	−379.5	64.5
NaOH (aq)	−470.1	−419.2	48.1

Sulfur	**ΔH°_f (kJ/mol)**	**ΔG°_f (kJ/mol)**	**S° (J/mol K)**
S (s, rhombic)	0	0	31.8
S (s, monoclinic)	0.3	0.1	33.0
S (g)	278.8	238.3	167.8
S_2^- (aq)	33.0	86.0	−15.0
S_8 (g)	102.0	50.0	431.0
S_2Cl_2 (g)	−18.4	−31.8	331.5
SF_6 (g)	−1,209.0	−1,105.3	291.8
H_2S (g)	−20.6	−33.6	205.8
SO_2 (g)	−296.8	−300.2	248.2
SO_3 (g)	−395.7	−371.1	256.8
$SOCl_2$ (g)	−212.5	−198.3	309.8

(*Continued*)

SO_4^{2-} (aq)	−909.0	−745.0	20.0
H_2SO_4 (l)	−814.0	−690.0	156.9
H_2SO_4 (aq)	−909.3	−744.5	20.1

Tin	**ΔH°_f (kJ/mol)**	**ΔG°_f (kJ/mol)**	**S° (J/mol K)**
Sn (s, white)	0	0	51.6
Sn (s, gray)	−2.1	0.1	44.1
$SnCl_4$ (l)	−511.3	−440.1	258.6
$SnCl_4$ (g)	−471.5	−432.2	365.8
SnO (s)	−285.0	−257.0	56.0
SnO_2 (s)	−580.7	−519.6	52.3
$Sn(OH)_2$ (s)	−561.0	−492.0	155.0

Titanium	**ΔH°_f (kJ/mol)**	**ΔG°_f (kJ/mol)**	**S° (J/mol K)**
Ti (s)	0	0	30.6
$TiCl_4$ (l)	−804.2	−737.2	252.3
$TiCl_4$ (g)	−763.2	−726.7	354.9
TiO_2 (s)	−939.7	−884.5	49.9

Uranium	**ΔH°_f (kJ/mol)**	**ΔG°_f (kJ/mol)**	**S° (J/mol K)**
U (s)	0	0	50.0
UF_6 (s)	−2,137.0	−2,008.0	228.0
UF_6 (g)	−2,113.0	−2,029.0	380.0
UO_2 (s)	−1,084.0	−1,029.0	78.0
U_3O_8 (s)	−3,575.0	−3,393.0	282.0
UO_3 (s)	−1,230.0	−1,150.0	99.0

(*Continued*)

Xenon	$\Delta H^o{}_f$ (kJ/mol)	$\Delta G^o{}_f$ (kJ/mol)	S^o (J/mol K)
Xe (g)	0	0	170.0
XeF_2 (g)	−108.0	−48.0	254.0
XeF_4 (s)	−251.0	−121.0	146.0
XeF_6 (g)	−294.0		
XeO_3 (s)	402.0		

Zinc	$\Delta H^o{}_f$ (kJ/mol)	$\Delta G^o{}_f$ (kJ/mol)	S^o (J/mol K)
Zn (s)	0	0	41.6
$ZnCl_2$ (s)	−415.1	−369.4	111.5
ZnO (s)	−348.3	−318.3	43.6
$Zn(OH)_2$ (s)	−642.0		
ZnS (s, wurtzite)	−193.0		
ZnS (s, zinc blende)	−206.0	−201.3	57.7
$ZnSO_4$ (s)	−983.0	−874.0	120.0

Regardless of the reaction, **Hess's law** states that the enthalpy change of a chemical reaction is the same regardless of the chemical path taken from reactants to products. If the reaction of interest is the sum of several other reactions, the individual heats of reaction must be added algebraically. In other words,

$$\Delta H_{\mathrm{RX}} = \sum \Delta H_{\mathrm{products}} - \sum \Delta H_{\mathrm{reactants}}$$

Note that this same principle also applies to the calculation of the Gibbs free energy change for chemical reactions.

Example 2.21

The standard heats of formation, ΔH_f^o, for NO_2 and N_2O_4 are as follows: ΔH_f^o [NO_2] = 33.9 kJ/mol and ΔH_f^o [N_2O_4] = −19.5 kJ/mol. Predict by calculation the heat of reaction, ΔH_{RX}, for the following reaction at standard conditions.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Solution

Use Hess's law.

$$\begin{aligned}\Delta H_{\text{RX}}^{\text{o}} &= \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} \\ &= \Delta H_f^{\,o}[\text{N}_2\text{O}_4] \ - \ 2\Delta H_f^{\,\text{o}}[\text{NO}_2] \\ &= \ (1.00 \text{ mol})(-19.5 \text{ kJ / mol}) \ - \ (2.00 \text{ mol})(33.9 \text{ kJ / mol}) \\ &= \ -87.3 \text{ kJ}\end{aligned}$$

Note that the negative sign means that the reaction is exothermic.

Example 2.22

Given the following reactions and data for ΔH^{o}:

$$N_2O_4\ (g) \rightarrow 2NO_2 \qquad \Delta H^{\text{o}}(\text{I}) = 87.30 \text{ kJ}$$

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2 \qquad \Delta H^{\text{o}}(\text{II}) = -114.14 \text{ kJ}$$

Compute $\Delta H_{\text{RX}}^{\text{o}}$ for the following reaction:

$$2NO\ (g) + O_2\ (g) \rightarrow N_2O_4\ (g)$$

Solution

First, recognize that, if the first given reaction (I) is reversed and added to the second reaction (II), the desired reaction is obtained, because the $2NO_2$ terms will be on opposite sides of the reaction and will therefore cancel. To do this, the sign of ΔH^{o}(I) must be changed from positive to negative, so the value becomes −87.30 kJ. Then, the two ΔH^{o} values must be added together. Thus:

$$\begin{aligned}\Delta H_{\text{RX}}^{\text{o}} &= \Delta H^{\text{o}}(\text{I}) + \Delta H^{\text{o}}(\text{II}) \\ &= -87.30 \text{ kJ} + (-114.14 \text{ kJ}) = -201.44 \text{ kJ}\end{aligned}$$

Another way to solve this problem is to use Hess's law and set the solution up as follows:

$$\begin{aligned}\Delta H_{\text{RX}}^{\text{o}} &= \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} \\ &= \Delta H_f^{\,o}[\text{N}_2\text{O}_4] \ - \ \{2\Delta H_f^{\,o}[\text{NO}] \ + \Delta H_f^{\,o}[\text{O}_2]\}\end{aligned}$$

The problem with this approach is that, although $\Delta H_f^{\,o}$ [O_2] = 0 and the value for $\Delta H_f^{\,o}$ [N_2O_4] is given in Example 2.22, the value for $\Delta H_f^{\,o}$ [NO] is unknown.

2.7.3 THE FIRST LAW AND THE CONSERVATION OF ENERGY

In understanding the laws of thermodynamics, it is useful to define *system* and distinguish it from *surroundings* very carefully. In general, there are three types of systems:

1. **Closed system—**a system that no mass enters or leaves.
2. **Isolated system—**a system that no mass or heat enters or leaves.
3. **Open system—**a system that mass or heat can enter or leave.

Furthermore, there are two kinds of *boundaries/walls* or processes:

1. **Diathermal walls**—walls that permit the transfer of heat between system and surroundings.
2. **Adiabatic walls**—walls that do not permit the transfer of heat between system and surroundings (e.g., good insulators).

The **first law of thermodynamics** can be stated in several ways. For example:

- The energy of the universe is constant. The total of the energy change of the system plus the energy change of the surroundings is, therefore, also constant.
- During a chemical or physical change in any defined system, energy can neither be created nor destroyed, but only changes form.

Expressed in mathematical terms:

$$\Delta \mathrm{E} = q - w \tag{2.27}$$

where

ΔE = the total internal energy change of the system,
q = the heat absorbed *by* the system *from* the surroundings,
w = the work done *by* the system *on* the surroundings.

For adiabatic processes, $q = 0$, so $\Delta E = -w$.

For isothermal changes in ideal gases, $\Delta E = 0$, since E is a function of temperature only.

For pressure-volume (i.e., mechanical) work of an idea gas (i.e., expansion or contraction):

If the pressure P is constant, then:

$$w = \int P\,\mathrm{d}V = P\,\Delta V \tag{2.28}$$

However, if P is not constant, then:

$$\begin{aligned} w &= \int P\,dV = \int \frac{nRT}{V}\,dV \\ &= nRT\,ln\frac{V_2}{V_1} \end{aligned} \tag{2.29}$$

ΔE and ΔH are related by the equation $\Delta H = \Delta E + P\,\Delta V$ at constant P.

Other types of thermodynamic work may include electrical and magnetic work.

Example 2.23

Ten moles of an ideal gas in a piston and cylinder assembly absorb 2,500 J of heat. The gas expands from 2.0 L to 8.5 L against a constant external pressure of 2.5 atm. What is the internal energy change of the system?

Solution

$$\begin{aligned} \Delta \mathrm{E} &= q - w = q - \mathrm{P}\,\Delta\mathrm{V} \\ &= 2{,}500\ \mathrm{J} - (2.5\ \mathrm{atm})(8.5\ \mathrm{L} - 2.0\ \mathrm{L}) \\ &= 2{,}500\ \mathrm{J} - 16.25\ \mathrm{L{\cdot}atm} \times (101.3\ \mathrm{J/L{\cdot}atm}) \\ &= 2{,}500\ \mathrm{J} - 1{,}646\ \mathrm{J} = 854\ \mathrm{J} \end{aligned}$$

Since the answer is positive, this amount of energy is *gained* by the system (and concurrently *lost* by the surroundings to the system in an equal amount).

2.7.4 THE SECOND LAW AND ENTROPY

The **second law of thermodynamics** may be expressed in several ways. For example:

- The **entropy, S,** that is, the randomness or disorder, of the universe either stays the same or increases, but never decreases.

- During a physical change or chemical reaction, the *total* **entropy change, ΔS_{total},** of the system plus the surroundings is either zero or positive, but never negative. The entropy change of a system, ΔS_{sys}, may be calculated as the reversible heat, q_{rev}, either gained or lost by a system, divided by the absolute temperature T:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} \tag{2.30}$$

Two consequences of the second law are as follows:

- The construction of a perpetual motion machine is impossible.
- It is impossible to build a heat engine with 100% efficiency.

A corollary of the second law, often referred to as the **zeroth law,** states that heat always flows from regions of hot to regions of cold *spontaneously*.

The term "reversible" refers to a process which is carried out over an infinitely slow series of steps such that each step is in equilibrium with a previous step. Practically speaking, other words for reversible are *gradual* or *extremely slow*.

Entropy is also a measure of the statistical disorder or randomness of a system. For all real or natural changes, which are spontaneous and irreversible, the entropy of a system increases, so the entropy *change*, ΔS, is positive, never zero or negative. On the grand scale, this means that the total is really the entire universe. Mathematically, this may be expressed as follows:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{universe}} \geq 0 \tag{2.31}$$

For phase transitions, $\Delta S_{\text{trans}} = \frac{q_{\text{trans}}}{T} = \frac{-\Delta H_{\text{trans}}}{T}$

where ΔH_{trans} may equal ΔH_{vap} or H_{fus}.

For the heating of any substance, without a phase transition, the heat gained or lost, *q,* may be expressed as

$$q = (\text{m})(C)(\Delta T) = \text{m}C\Delta T \tag{2.32}$$

where

m = the mass of the substance in grams or moles,
C = the specific heat or heat capacity in suitable units,
ΔT = the change in temperature in degrees Celsius or kelvins.

For other processes involving changes in temperature and/or volume:

$$\Delta S = C_v \ln\frac{T_2}{T_1} + n\text{R} \ln\frac{V_2}{V_1} \tag{2.33}$$

Example 2.24

One mole of an ideal gas expands reversibly and isothermally from an initial volume of 2 L to a final volume of 20 L. Calculate the entropy change, in calories/kelvin, of the system and the surroundings.

Solution

Since this process is isothermal, $T_1 = T_2$, use $\Delta S = n\text{R} \ln V_2/V_1$. Then:

$$\begin{aligned}\Delta S_{\text{sys}} &= (1.00\,\text{mol})(1.99\,\text{cal}/\text{K}\cdot\text{mol})\ \text{In}\left(\frac{20\ \text{L}}{2.0\ \text{L}}\right)\\ &= 4.58\ \text{cal}/\text{K}\end{aligned}$$

Since this is a reversible process:

$$\Delta S_{\text{sys}} = -\Delta S_{\text{surr}} = -4.58\,\text{cal/K}$$

Example 2.25

Calculate the entropy change when 100 g of water vaporizes at 100° C.

Solution

This is a phase transition. Use $\Delta S_{\text{trans}} = \Delta H_{\text{vap}}/T$ (mentioned above for phase transitions) where $\Delta H_{\text{vap}} = 540$ cal/g and $T = 373$ K. Then:

$$\begin{aligned}\Delta S &= \frac{\left(540\,\frac{\text{cal}}{\text{g}}\right)(100\,\text{g})}{373\,\text{K}}\\ &= 145\ \text{cal}/\text{K}\end{aligned}$$

2.7.5 THE THIRD LAW AND ABSOLUTE ZERO

The **third law of thermodynamics** provides a basis for determining the absolute entropy of a substance or system. There are different ways of stating it. According to Max Planck, one way to state is that a perfect crystal has zero entropy at a temperature of absolute zero. A perfect crystal is one in which all of the atoms are aligned flawlessly with no defects of any kind in the crystalline structure. All of the atoms are motionless and have zero kinetic energy. This formulation is largely a statistical interpretation and involves the study of statistical mechanics, which is beyond the scope of this book. Nevertheless, it is postulate, like the other two laws of thermodynamics, and its validity rests on experiment. However, since there are no means available to measure absolute entropies directly, it remains largely a theoretical principle.

Another common interpretation of the third law states that it is impossible to reach the state of absolute zero in a finite series of steps. This is entirely consistent with Planck's statement of the third law.

2.7.6 GIBBS FREE ENERGY AND THE SPONTANEITY OF A REACTION

The Gibbs free energy change, ΔG, is defined as:

$$\Delta G = \Delta H - T\,\Delta S \tag{2.34}$$

Its chief value is that it is an unequivocal measure and indication of a reaction's spontaneity. It includes both an enthalpy term, ΔH, and an entropy term, ΔS.

Every reaction seeks to simultaneously reach a state of minimum energy and a state of maximum entropy. Thus, if the sign of ΔG is negative, the reaction proceeds spontaneously as written, though kinetically, it may be very slow; if positive, the *reverse* reaction proceeds spontaneously.

For equilibrium reactions, ΔG can be expressed as

$$\Delta G = -\mathrm{R}T \ln \mathrm{K_c} \;\; \text{in general, for all reactions} \tag{2.35}$$

$$\Delta \mathrm{G} = -\mathrm{R}T \ln \mathrm{K_p} \;\; \text{for gas-phase reactions} \tag{2.36}$$

Example 2.26

Airborne, particulate sulfur, S (s), may react with hydrogen gas, H_2 (g) to produce H_2S gas, according to the following reaction:

$$\mathrm{H_2\,(g)\; +\; S\;(s) \rightarrow H_2S(g)}$$

Given $\Delta H_f^\circ = -20.2$ kJ/mol and $\Delta S_f^\circ = +43.1$ J/K · mol.

A. Compute ΔG° for the reaction.
B. Tell whether the reaction is spontaneous.

Solution

A. Use $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$. Note that the ΔG° that will be computed is really ΔG_f°. At standard conditions, $T = 298$ K, and all quantities are 1.0 mol.

$$\Delta G^\circ = -20.2 \times 10^3 \text{ J} - (298 \text{ K})(+43.1 \text{ J/K})$$

$$= -33{,}908 \text{ J} = -33.9 \text{ kJ}$$

B. Since the sign of ΔG is negative, the reaction is spontaneous as written.

Example 2.27

At 1,500°C, carbon monoxide reacts with hydrogen gas as shown in the reaction below. This is one way to synthesize methanol and eliminate carbon monoxide at the same time.

$$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$$

It is known that $K_p = 1.4 \times 10^{-7}$.

A. Compute ΔG for the reaction.
B. State whether the reaction is spontaneous.

Solution

A. Use $\Delta G = -RT \ln K_p$. Then,

$$\Delta G = -(8.31 \text{ J/K·mol})(1{,}773 \text{ K}) \ln(1.4 \times 10^{-7})$$

$$= 233 \text{ J/K·mol}$$

B. Since the sign of ΔG is positive, this reaction is *not* spontaneous as written.

2.8 ELECTROCHEMISTRY AND RED-OX REACTIONS

2.8.1 BASIC CONCEPT

One category of chemical reactions described briefly in Section 1.9.2 is oxidation-reduction reactions, or "red-ox" reactions for short. Oxidation-reduction ("red-ox") reactions are reactions in which one substance is oxidized while another is simultaneously reduced. The processes of oxidation and reduction can be defined as follows. Oxidation is the loss of electrons, while reduction is the gain of electrons. However, diagnostically speaking, a substance is oxidized or reduced, respectively, if any *one* of the following conditions is met:

Oxidation

- Loss of electrons
- Gain of oxygen atoms
- Loss of hydrogen atoms

Reduction

- Gain of electrons
- Loss of oxygen atoms
- Gain of hydrogen atoms

Consider the arrangement shown in Figure 2.2. This arrangement is known as an **electrochemical cell**, and the underlying electrochemical reaction involves simultaneous oxidation and reduction reactions. Electrochemical cells are the basis of operation of all batteries. If the reactions and current flow are spontaneous, as in any battery, the cell is called a **voltaic** or **galvanic cell.** If, instead, electrical energy must be supplied, the cell is called an **electrolytic cell,** and the process is known as **electrolysis.**

An electrochemical cell is comprised of two **half-cells.** In one, called the **anode, oxidation** occurs; in the other, called the **cathode, reduction** occurs. Each reaction is called a **half-reaction.** The sum of the two half-reactions is the overall or net reaction. The rusting of iron or the corrosion of any metal involves an **oxidation–reduction** process, with a net electromotive potential.

Some useful physical measurements and their units in electrochemical cells include the volt (V), the electron volt (eV), the coulomb (C), and the ampere (A). Since 1 volt = 1 joule per coulomb, and 1 ampere = 1 coulomb per second, then (current in amperes) × (time in seconds) = total charge transferred in coulombs.

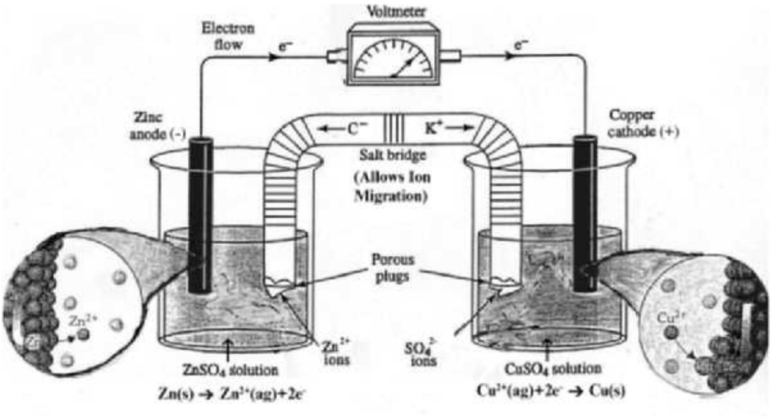

Figure 2.2. A copper–zinc electrochemical galvanic cell

In addition, (potential in volts) × (charge in coulombs) = total energy produced or used in joules. See equations 2.43 through 2.49 for a summary of useful quantitative relationships for electrochemical cells.

2.8.2 THE NERNST EQUATION

The electromotive potential developed by the cell diagramed in Figure 2.2 is very useful. It can be harnessed and serve as the basis of battery power. In fact, pairs of different metals can be similarly arranged to produce a variety of desired voltages.

When all substances used in the cell are in their standard states, the net voltage is the simple sum of the individual cell potentials or voltages listed in Table 2.5. Standard states mean that all metals are pure, their starting salt concentrations in solution are 1.00 molar, and the ambient or operating temperature is 25°C. Such a situation is outlined in the following section, using the diagram in Figure 2.2. A specific set of conditions is given in Example 2.28.

However, when nonstandard conditions exist, another equation must be used to calculate the net potential of the electrochemical cell. Nonstandard conditions usually refer to operating temperatures other than 25°C, or concentration values of dissolved metal species other than 1.00 molar. The law describing the relationship between the concentrations of ionic solutions and the voltage produced in the net reaction is called the **Nernst equation** and is expressed as follows:

$$E_{\text{net}} = E_{\text{net}}{}^{\circ} - \frac{\mathrm{R}T}{nF}\ \ln Q \tag{2.37}$$

where

E°_{net} = the total or net cell potential in volts obtained by the addition of the two potentials corresponding to the two standard half-cell reactions under standard conditions.

E_{net} = the total or net cell potential in volts of the cell operating under nonstandard conditions, usually due to a temperature other than 25°C, or concentration values of dissolved metal species other than 1.00 molar.

R = the gas constant = 8.31 J/K·mol

T = the absolute temperature in kelvins

F = the Faraday constant = 96,485 C/mol electrons

n = the number of moles of electrons transferred per unit reaction

Q = the ratio of molar concentrations of products to molar concentrations of reactants, for all (aq) or (g) species in solution [species which have an (s) or (l) state are excluded]. See the earlier discussion on equilibrium concepts in Section 2.1.

Note that the term "E_{net}" may be referred to as either the cell potential or the electromotive force potential, or simply the EMF of the cell.

For the condition where T = 25°C = 298 K, and since ln Q = 2.303 log Q, the Nernst equation can be simplified to:

$$E_{\text{net}} = E_{\text{net}}{}^{\circ} - \frac{0.0591}{n} \log Q \tag{2.38}$$

This array of choices of solution concentration can produce seemingly endless combinations of cell arrangements and variations, and generate exactly desired voltages for very specific applications. Note that when standard conditions are met, the log Q term vanishes, and the Nernst equation simplifies to $E_{\text{net}} = E^{\circ}_{\text{net}}$. An example of this type of problem is given in Example 2.29.

Table 2.5 shows the standard reduction reactions of metals, along with selected nonmetals, and their corresponding potentials, relative to the standard hydrogen electrode (whose reduction potential is taken as zero) at 25°C. More extensive tables of reduction potentials organized according to the presence of acidic and alkaline conditions can be found in the *Handbook of Chemistry and Physics*. It is important to note that reduction reactions and potentials depend on the pH of solution, as well as the presence of any complexing agents. This listing is often referred to as the **electromotive series,** and the reduction potentials given as the *E*° values in volts. If the *E*° value listed is positive, the reaction is spontaneous as written. If negative, the reverse reaction is spontaneous. The superscript zero refers to standard conditions, that is, a temperature of 25°C, a concentration of 1.00 M for any ions present in solution, and a partial pressure of 1.00 atm for any gases present.

Table 2.5. The electromotive series expressed as standard reduction potentials at STP

E° (volts)	Half-Cell Reaction
+2.87	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$
+2.08	$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O$
+2.05	$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$
+1.82	$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$
+1.77	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O$
+1.695	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$
+1.69	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$
+1.63	$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$
+1.51	$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq)$
+1.49	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$
+1.46	$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$
+1.44	$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$
+1.42	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$
+1.36	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O$
+1.24	$O_3(g) + H_2O + 2e^- \rightleftharpoons O_2(g) + 2OH^-(aq)$
+1.23	$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$
+1.20	$Pt^{2+}(aq) + 2e^- \rightleftharpoons Pt(s)$
+1.07	$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O$

(*Continued*)

E° (volts)	Half-Cell Reaction
+0.94	$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons HNO_2(aq) + H_2O$
+0.91	$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$
+0.87	$HO_2^-(aq) + H_2O + 2e^- \rightleftharpoons 3OH^-(aq)$
+0.80	$NO_3^-(aq) + 4H^+(aq) + 2e^- \rightleftharpoons 2NO_2(g) + 2H_2O$
+0.80	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$
+0.69	$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$
+0.54	$I_2(s) + 2e^- \rightleftharpoons 21^-(aq)$
+0.49	$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$
+0.45	$SO_2(aq) + 4H^+(aq) + 4e^- \rightleftharpoons S(s) + 2H_2O$
+0.401	$O_2(g) + 2H_2O + 4e^- \rightleftharpoons 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
+0.27	$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$
+0.25	$PbO_2(s) + H_2O + 2e^- \rightleftharpoons PbO(s) + 2OH^-(aq)$
+0.2223	$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$
+0.172	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$
+0.169	$S_4O_6^{2-}(aq) + 2e^- \rightleftharpoons 2S_2O_3^{2-}(aq)$
+0.16	$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$
+0.15	$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$
+0.14	$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$
+0.07	$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$
0.00	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$
−0.13	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$
−0.14	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$
−0.15	$Agl(s) + e^- \rightleftharpoons Ag(s) + 1^-(aq)$
−0.25	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$
−0.28	$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$
−0.34	$In^{3+}(aq) + 3e^- \rightleftharpoons ln(s)$
−0.34	$Tl^+(aq) + e^- \rightleftharpoons Tl(s)$

(*Continued*)

E° (volts)	Half-Cell Reaction
−0.36	$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$
−0.40	$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$
−0.56	$Ga^{3+}(aq) + 3e^- \rightleftharpoons Ga(s)$
−0.58	$PbO(s) + H_2O + 2e^- \rightleftharpoons Pb(s) + 2OH^-(aq)$
−0.74	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$
−0.81	$Cd(OH)_2(s) + 2e^- \rightleftharpoons Cd(s) + 2OH^-(aq)$
−0.83	$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$
−0.88	$Fe(OH)_2(s) + 2e^- \rightleftharpoons Fe(s) + 2OH^-(aq)$
−0.91	$Cr^{2+}(aq) + e^- \rightleftharpoons Cr(s)$
−1.16	$N_2(g) + 4H_2O + 4e^- \rightleftharpoons N_2O_4(aq) + 4OH^-(aq)$
−1.18	$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$
−1.216	$ZnO_2^-(aq) + 2H_2O + 2e^- \rightleftharpoons Zn(s) + 4OH^-(aq)$
−1.63	$Ti^{2+}(aq) + 2e^- \rightleftharpoons Ti(s)$
−1.66	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$
−1.79	$U^{3+}(aq) + 3e^- \rightleftharpoons U(s)$
−2.02	$Sc^{3+}(aq) + 3e^- \rightleftharpoons Sc(s)$
−2.36	$La^{3+}(aq) + 3e^- \rightleftharpoons La(s)$
−2.37	$Y^{3+}(aq) + 3e^- \rightleftharpoons Y(s)$
−2.37	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$
−2.71	$Na^+(aq) + e^- \rightleftharpoons Na(s)$
−2.76	$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$
−2.89	$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$
−2.90	$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$
−2.92	$Cs^+(aq) + e^- \rightleftharpoons Cs(s)$
−2.92	$K^+(aq) + e^- \rightleftharpoons K(s)$
−2.93	$Rb^+(aq) + e^- \rightleftharpoons Rb(s)$
−3.05	$Li^+(aq) + e^- \rightleftharpoons Li(s)$

The listing is also referred to as the **activity series** of metals, since they indicate which metal is more likely, relative to another, to release its electrons, oxidize, and react. The reactions posted are sometimes referred to as **half-cell reactions**. For example, the metal lithium has the highest *negative* $E°$ value, −3.045 V, while magnesium has an $E°$ value of −2.363 V. Therefore, elemental lithium will oxidize and react more easily than elemental magnesium. The nonmetal fluorine has the highest *positive* $E°$ value, +2.87 V, and is thus easiest to reduce. In other words, a large negative $E°$ value means that the reactant is a good reducing agent, and a large positive $E°$ value indicates a good oxidizing agent.

2.8.3 A SIMPLE ELECTROCHEMICAL CELL

Consider once again the copper–zinc electrochemical cell shown in Figure 2.2.

In the right half-cell, the cathode, Cu^{2+} ions in solution are being reduced to Cu^0, indicating solid copper metal deposit on the Cu cathode. In the left half-cell, the anode, Zn^0 or solid zinc is being oxidized to Zn^{2+} ions, which dissolve in solution. The anions—SO_4^{2-} (aq)—are spectator ions and do not participate in the reaction. The salt bridge is necessary to maintain electrical neutrality and retard polarization.

The short-hand notation for this cell is as follows:

$$\mathrm{Zn(s)} \mid \mathrm{ZnSO_4\,(aq)(1.00\ M)} \| \mathrm{CuSO_4\,(aq)(1.00\ M)} \mid \mathrm{Cu(s)} \qquad (2.39)$$

It is understood that the anode cell, where oxidation occurs, is written first and is separated by a double vertical line from the cathode cell, where reduction occurs. Single vertical lines separate the solid electrode from the aqueous solution into which it is immersed. Concentrations of the solutions are expressed in moles per liter in parentheses.

The two half-reactions, followed by the **net reaction,** can be written as follows:

At Cathode

$$\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu^0(s)} \qquad E° = 0.337\,\mathrm{V} \qquad (2.40)$$

At Anode

$$\mathrm{Zn^0(s) \rightarrow Zn^{2+}(aq) + 2e^-} \qquad E° = 0.763\,\mathrm{V} \qquad (2.41)$$

Net Reaction

$$\mathrm{Cu^{2+}(aq)} + \cancel{2e} + \mathrm{Zn^0(s)} \rightarrow \mathrm{Cu^0(s)} + \mathrm{Zn^{2+}(aq)} + \cancel{2e} \qquad E_{\mathrm{net}}{}^{\circ} = 1.100\ \mathrm{V}$$

Or finally,

$$\mathrm{Cu^{2+}(aq)} + \mathrm{Zn^0(s)} \rightarrow \mathrm{Cu^0(s)} + \mathrm{Zn^{2+}(aq)}\ E_{\mathrm{net}}{}^{\circ} = 1.100\ \mathrm{V} \quad (2.42)$$

Note that the electrons from the two half reactions exactly cancel each other, and do not appear in the final net reaction. If this cancellation of electrons does not happen automatically, one or both of the half-reactions must be multiplied by a suitable coefficient (i.e., an integer) or coefficients to obtain the exact cancellation of electrons. Note also that the positive value for $E_{\mathrm{net}}{}^{\circ}$ indicates that this reaction proceeds **spontaneously** and the cell produces 1.100 V under standard conditions.

Also note that the E^{o} value at the cathode represents a reduction potential and may be written as $E^{\mathrm{o}}{}_{\mathrm{red}}$, while the $\mathrm{E^o}$ value at the anode represents an oxidation potential and may be written as $E^{\mathrm{o}}{}_{\mathrm{ox}}$. This convention may be used in other reference manuals or textbooks.

Useful Quantitative Relationships

1 mole of electrons (e^-) = 96,485 coulombs (C) (2.43)

charge (C) = current (C/sec) × time (sec) (2.44)

1 ampere (A) = 1 coulomb/1 second (2.45)

1 volt (V) = 1 joule (J)/1 coulomb (2.46)

Faraday constant F = 96,485 coulombs/mole e^- (2.47)

Gas constant R = 8.31 joules/kelvin · mole (2.48)

Number of moles of e^- = (current × time)/F (2.49)

Example 2.28

Consider the electrochemical cell with the following net reaction, which is observed to proceed spontaneously. All species are in their standard states, that is, concentrations of dissolved species are 1.00 molar, and T = 25°C.

$$\mathrm{Mg(s)} + \mathrm{Sn^{2+}(aq)} \rightarrow \mathrm{Mg^{2+}(aq)} + \mathrm{Sn(s)}$$

A. Using Table 2.5, write the two half-reactions with their respective $E°$ values.
B. Indicate which species is oxidized and which is reduced.
C. Identify the anode and cathode.
D. Compute $E_{net}°$.
E. Confirm that the reaction proceeds spontaneously.

Solution

A. $\mathrm{Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-} \qquad E° = 2.370\ \mathrm{V}$

$\mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)} \qquad E° = -0.140\ \mathrm{V}$

B. Mg (s) is oxidized to Mg^{2+} (aq), while Sn^{2+} (aq) is reduced to Sn (s).
C. The anode is the electrode where oxidation takes place, while the cathode is the electrode where reduction takes place. Since Mg is oxidized, the half-cell containing the Mg electrode and Mg^{2+} (aq) solution must be the anode.

Similarly, the cathode is the half-cell containing the Sn electrode dipped into Sn^{2+} (aq) solution.
D. Adding the two half-cell potentials determined in **A** gives $E_{net}° = 2.230$ V.
E. Since $E_{net}°$ is a positive number, the net reaction must proceed spontaneously.

Example 2.29

Consider the reaction in Example 2.28. Instead of standard conditions of 1.00 M concentrations for each solution, assume now that the Mg^{2+} (aq) solution is 0.850 M and that the Sn^{2+} (aq) solution is 0.0150 M. Find the $E_{net}°$ under these conditions, assuming $T = 25.0°C$.

Solution

Since this is under nonstandard conditions, the Nernst equation applies. However, use the simplified version of this equation, equation 2.38, since $T = 25.0°C$.

$$E_{net} = E_{net}° - \frac{0.0591}{n} \log Q$$

In this case, $n = 2$, since 2 mol of electrons are exchanged in the *net* reaction.

Also, by examining the net reaction, Q is found to be:

$$Q = \frac{\left[\mathrm{Mg^{2+}(aq)}\right]}{\left[\mathrm{Sn^{2+}(aq)}\right]} = \frac{0.850\ \mathrm{M}}{0.0150\ \mathrm{M}}$$

$E_{\mathrm{net}}°$ was calculated in **D** of Example 2.28 as 2.230 V. Substitution now gives:

$$\begin{aligned} E_{\mathrm{net}} &= 2.230\ \mathrm{V} - \frac{0.0591}{2}\log\frac{0.850\ \mathrm{M}}{0.0150\ \mathrm{M}} \\ &= 2.178\ \mathrm{V} \end{aligned}$$

Example 2.30

Compute the Gibbs free energy change, ΔG, for the cell in Example 2.29.

Solution

$$\begin{aligned} \Delta G &= nFE_{\mathrm{net}} \\ &= -(2\ \mathrm{mol\ e^-})(96,485\mathrm{C/mol\ e^-})(2.178\ \mathrm{V}) \\ &= -420,290\ \mathrm{J\ or} -420.3\ \mathrm{kJ} \end{aligned}$$

Example 2.31

Consider the following cell reaction, in which all species are standard-state conditions:

$$\mathrm{Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)}$$

A. Predict the effect on the electromotive potential of this cell of adding NaOH solution to the hydrogen half-cell until pH = 7.
B. Compute the number of coulombs required to deposit 4.20 g of Cu (s) in the copper half-cell.
C. How long in seconds will this deposition take, if the measured current is 4.00 A?

Solution

A. Refer to the simplified Nernst equation, equation 2.38. The EMF is the E_{net}:

$$E_{\mathrm{net}} = E_{\mathrm{net}}° - \frac{0.0591}{2}\log\frac{[\mathrm{H^+}]^2}{[\mathrm{Cu^{2+}}]}$$

If NaOH (aq) is added, H^+ ions (aq) will be neutralized, thereby raising the pH. [H^+ (aq)] will decrease, reducing the magnitude of the log term, which is subtracted from $E_{net}°$. This, in turn, will increase the E_{net} or the emf of the cell.

B. First, compute the number of electrons that must be transferred to deposit 4.20 g of Cu (s). Then, recall that 1.00 mol of Cu^{2+} (aq) is deposited as Cu (s) for every 2.0 mol of electrons used, and that the Faraday constant F = 96,485 C/1.00 mol electrons. Thus, first,

$$4.20\ \text{g Cu}(\text{s})\left(\frac{1.00\ \text{mol Cu}}{63.5\ \text{g Cu}}\right) = 0.06614\ \text{mol Cu}(\text{s})\ \text{deposited}$$

Next, use this result to find the moles of electrons:

$$0.06614\ \text{mol Cu}(\text{s})\left(\frac{2\ \text{mol e}^-}{1.00\ \text{mol Cu}(\text{s})}\right) = 0.1323\ \text{mol e}^-$$

Finally, calculate coulombs from the moles of electrons:

$$0.1323\ \text{mol e}^-\left(\frac{96{,}485\ \text{C}}{1.00\ \text{mol e}^-}\right) = 1.28\times10^4\ \text{C}$$

C.

$$\begin{aligned}\text{time, } t(\text{sec}) &= \frac{\text{charge}(\text{C})}{\text{current}\left(\text{C}/\text{sec}\right)} \\ &= \frac{1.28\times10^4\ \text{C}}{4.00\ \text{A}} \\ &= 3.20\times10^3\ \text{sec}\end{aligned}$$

This is about 53 min or a little less than 1.0 hr.

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CHAPTER 3

ORGANIC CHEMISTRY AND ESSENTIALS OF POLYMER CHEMISTRY

Many molecules fall into the category of organic molecules. With a few exceptions, all molecules that contain carbon are considered organic molecules. These molecules have a great deal to do with living organisms (thus the name organic), but are just as often found in other places. Organic compounds are present in oils, paints, soaps, surfactants, solvents, plastics, fuels, and numerous other products employed in everyday life as well as in industrial settings. Being able to identify organic molecules can be important for a variety of reasons, most importantly for safety.

Carbon atoms are unique among atoms in that they can be easily bonded to each other in a dizzying array of different arrangements. Different arrangements lead to different properties. Some of these differences can be minor, as to how hot something burns perhaps, but sometimes a small variation can lead something from being relatively safe to being very toxic. A good example might be that of methanol and ethanol. Although both molecules are clear liquids at room temperature, methanol (CH_3OH) is quite toxic, while ethanol (C_2H_5OH) is commonly consumed in "alcoholic" beverages (though is not quite completely safe either). As a side note, "alcoholic" is in quotes because, as will soon be seen, "alcohol" has a particular meaning in chemistry that does not exactly match its common day use.

Identification of organic molecules is governed by the IUPAC System (International Union of Pure and Applied Chemistry). This system allows for a systematic way to name any organic compound. This is necessary due to the very large number of ways in which carbon-containing molecules can be built, and because sometimes more than one name could possibly be constructed. The rules are strict for easy identification. Popular fiction sometimes breaks these rules. (For example, in the computer game "Star Wars: The Old Republic," a quest item is called 3,5,7-trichloroheptane. You should, by the end of this chapter, be able to identify the molecule, and explain why IUPAC appears to not apply in a galaxy far, far away.)

3.1 ALKANES—SIMPLE CARBON CHAINS

The two main categories of naming are for compounds that are aliphatic, that is straight chains or saturated or partially unsaturated cycles, and aromatic for those that are a special type of unsaturated cycles. As may be recalled from Chapter 1, neutral carbons always form four bonds. If all carbon forms only single bonds to other carbons in a compound, that type of carbon compound is called saturated. If there are any double or triple bonds, those will be unsaturated. For now, the simplest of the cases will be considered in which only saturated straight chain carbon compounds, or alkanes, are present.

Alkanes are the basis for the names of many organic compounds, so it is important to remember their names. The name of each compound is composed of a prefix (alk~) to indicate the number of carbons, and a suffix (~ane) to indicate that the compound is fully saturated. Table 3.1 shows a list of these names for the first 10 alkanes.

Table 3.1. Alkane nomenclature

Name	Prefix	Suffix	Number of C	Formula
methane	meth~	~ane	1	CH_4
ethane	eth~	~ane	2	C_2H_6
propane	prop~	~ane	3	C_3H_8
butane	but~	~ane	4	C_4H_{10}
pentane	pent~	~ane	5	C_5H_{12}
hexane	hex~	~ane	6	C_6H_{14}
heptane	hept~	~ane	7	C_7H_{16}
octane	oct~	~ane	8	C_8H_{18}
nonane	non~	~ane	9	C_9H_{20}
decane	dec~	~ane	10	$C_{10}H_{22}$

In this table some of the prefixes may be familiar from the Chapter 1 section on naming compounds. Although the first four compounds, methane, ethane, propane, and butane, have names tied to the history of the compound, the 5-carbon compound and on, have prefixes that are ancient Greek numerical prefixes. Octane, which is a major component of gasoline and is associated with octane rating, may be noted here. (It should now be possible to develop an idea of what that compound from a galaxy far, far away looks like, although further clarification is still needed.)

3.1.1 DRAWING ORGANIC MOLECULES

The depiction of organic molecules is critical to their discussion. In organic chemistry a particular short hand is used, called line notation, to simplify structures with many carbons and hydrogens. In general, lines are used to denote bonding pairs of electrons. As shown in Figure 3.1, one line is two electrons shared by neighboring atoms. Two parallel lines, like an equation sign, indicate a double bond, or four shared electrons. A set of three parallel lines between two atoms indicates a triple bond, or six shared electrons.

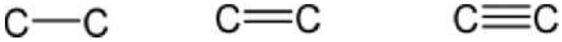


Figure 3.1. Bonds in line notation

Because there are so many carbons involved in organic chemistry, and most carbons have some hydrogens attached to them, two further simplifications are made. One, instead of writing each carbon, the atomic symbol for them is generally omitted. If multiple carbons are omitted in a row, then the line is drawn in a zig-zag fashion, with each angle break in the line indicating the presence of a carbon. Additionally, hydrogen atoms are usually (but not always) omitted. They are not indicated in any way. It is assumed that every carbon will have four bonds, and any bonds not drawn already are to a hydrogen atom. The process of simplifying a molecular structure is shown in Figure 3.2.

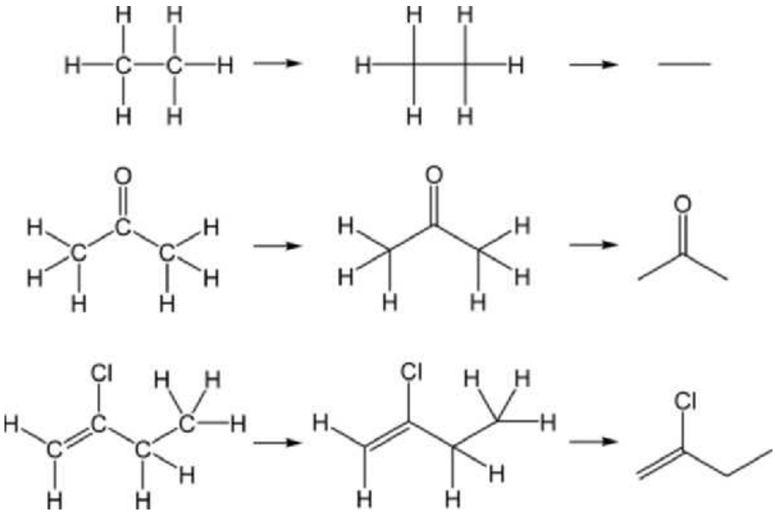


Figure 3.2. Simplifying molecular structures to line notation. Top: ethane. Middle: acetone (formal name 2-propanone). Bottom: 2-chloro-1-butene

3.2 FUNCTIONAL GROUPS

The reason that there are so many carbon compounds is that the alkanes listed above can be varied very easily, with simple substitutions, in a nearly endless number of ways. Consider the fairly simple case of a propane molecule with two hydrogens replaced by chlorines to yield dichloropropane, as shown in Figure 3.3.

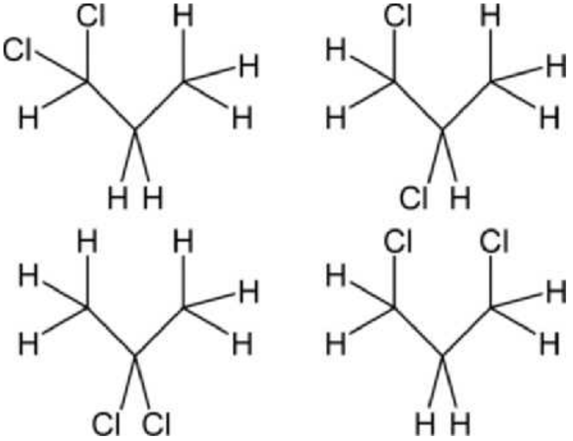


Figure 3.3. Isomers of dichloropropane

Note that all four of these compounds have three carbons in a chain (propane) and have two chlorines (dichloro). They are, however, not the same compound, as the locations of the chlorines are different in each case. A systematic way to distinguish between all four of these is needed, and there is also need to avoid redundancy. For instance, the first compound is the same as the one shown in Figure 3.4, except rotated 180 degrees. They are, in reality, the same compound, and it should be possible to know how to name them the same way.

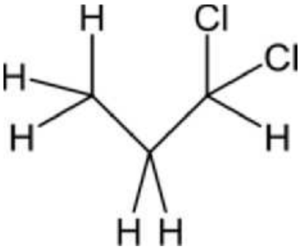


Figure 3.4. 1,1-Dichloropropane. Despite appearances, this molecule is the same as the one in the top left of Figure 3.3

3.2.1 ALKENES

Although it could be argued whether alkenes are strictly speaking "functional groups," it is still necessary to name them, and they tend to behave differently from their alkane counterparts. An alkene is an alkane with a double bond (or possibly multiple double bonds) in it. Alkenes are unsaturated. That is, the compound has less than the maximum number of hydrogens that could be attached to the carbons. Alkenes are named by replacing the ~ane suffix with an ~ene suffix to indicate the double bond. Table 3.2 illustrates this concept.

Table 3.2. Alkene nomenclature

Name	Prefix	Suffix	Number of C	Formula
ethene	eth~	~ene	2	C_2H_4
propene	prop~	~ene	3	C_3H_6
butene	but~	~ene	4	C_4H_8

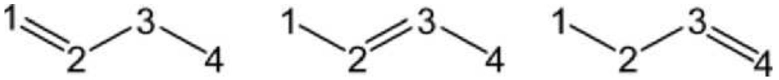


Figure 3.5. Isomers of butane. The first and last isomers are identical, and the first, where the double bond is between 1 and 2, is the preferred choice for naming.

Notice that for butene, there are two different ways to draw a structure, as seen in Figure 3.5. This becomes a problem in identifying the best structure. (For propene, care is necessary, as it can be noted that the two possible structures are really just rotations of the same structure.)

IUPAC nomenclature notes the following rules. For different possible arrangements, number the carbons on the molecule in question in order. For alkenes, identify the first of the carbons involved in the double bond as a numerical value before the English name, and followed by a hyphen; for example, 2-pentene. The correct IUPAC name is the one where the lowest possible values are used for identifying the points where there are double bonds. Figure 3.5 illustrates this point.

Consider the butenes in Figure 3.5. The first would be 1-butene, as the double bond originates at the first carbon. The second would be 2-butene as the double bond originates at the second carbon. Now consider 3-butene. This molecule, 3-butene, would not describe the second structure, as 3-butene implies that the double bond is between carbon 3, and the next carbon in line, carbon 4. Considering the structure of 3-butene, however, it can be seen that it is the same as 1-butene, that there are four carbons in a row, and there is a double bond at the end. They are the same molecule, just rotated in space. Since names with the lowest numbers are preferred, 1-butene is the correct name, not 3-butene.

For molecules with more carbons, there become more and more ways to arrange the double bonds. There are two ways to make pentene, three ways to make hexene and heptene, and so on.

3.2.2 ALKYNES

Alkynes are much like alkenes, except instead of a double bond, there is a carbon-carbon triple bond in the compound. A commonly encountered alkyne is acetylene, used in acetylene-welding torches. Acetylene is the trivial name for ethyne. Relying on an understanding from the previous section, ethyne should be an ethane-based compound with a triple bond in it. The same rules apply as before, as shown in Table 3.3. The location of the triple bond, if ambiguous, is named by the first of the carbons involved in the triple bond in the structure.

Table 3.3. Alkyne nomenclature

Name	Prefix	Suffix	Number of Carbons	Formula
ethyne	eth~	~yne	2	C_2H_2
propyne	prop~	~yne	3	C_3H_4
butyne	but~	~yne	4	C_4H_4
pentyne	pent~	~yne	5	C_5H_8

3.2.3 OTHER GROUPS

Other substituents are frequently encountered in carbon compounds. Halogens, especially chlorine, are particularly common in a variety of solvents used in a wide range of industrial applications. Any time an atom other than a hydrogen is attached to a carbon, it is referred to as a functional group. Functional groups have to be identified much the same way as alkenes and alkynes. They are named, and then located by the number of the carbon to which they are attached. In a fit of brilliance (and to make things orderly) IUPAC nomenclature puts the numbers to locate the atoms before the name, then names the nonhydrogen atoms, and then identifies the carbon chain to which they are attached. Thus the names look something like 1,1,2-trichloropentane (a pentane with three chlorines, two chlorines on the first carbon and one on the second).

Example 3.1

Name the compounds shown in Figure 3.6. These are the same compounds as in Figure 3.3, reproduced here for easy reference.

Solution

These compounds can be systematically named. First it is necessary to identify the alkane from which each is derived. Then the number and type of functional groups is identified. Then their locations are identified. And finally, the name can be assembled. In each case, there are three carbons in the chain, so propane is the base compound. There are two chlorines in each case, thus yielding dichloropropane. Compound (a) is 1,1-dichloropropane. Compound (b) is 1,2-dichloropropane. Compound (c) is 2,2-dichloropropane. Compound

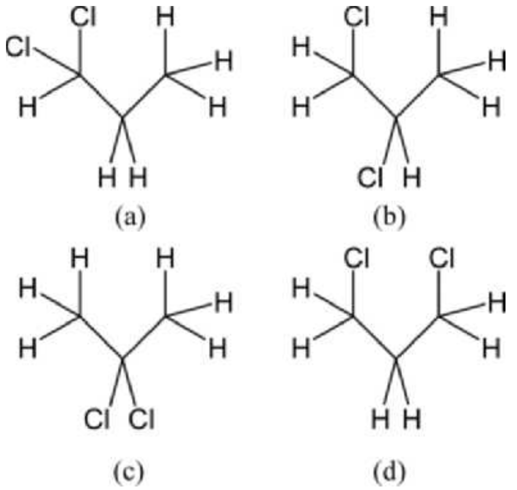


Figure 3.6. Name these molecules

(d) is 1,3-dichloropropane. Remembering from earlier discussion that the preferred name is the one with the lowest numbers, 3,3-dichloropropane is really 1,1-dichloropropane, and 2,3-dichloropropane would be 1,2-dichloropropane.

While many substituents are named as above, others will be named at the end of a compound instead. One example is that of alcohols. Alcohols in chemical terms are a class of related compounds that include an –OH group attached to a carbon atom. Ethanol is a particular example. As might be guessed by now, this is a molecule in which an ethane is modified by adding an –OH to one of the carbons. Ethanol is what on an everyday basis we call "alcohol." For these kinds of molecules, the rule is, the ending ~e is dropped from the base alkane, and is replaced with a suffix indicating the name of the functional group added.

There is a third way some compounds are named. In these cases, carbon chains are viewed as being attached to the functional group rather than the functional group being attached to the carbon chain. To indicate this, the root name is modified by the suffix ~yl to indicate that there is a missing hydrogen at the end of the chain, and that the carbons are attached to something else. For example, methyl indicates that CH_3 is attached to something else. One example is a chemical recently popularized by a television show, methylamine (Figure 3.7):

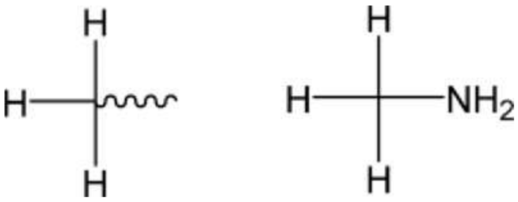
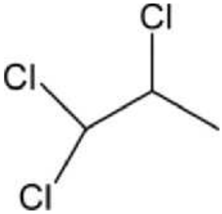
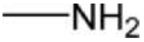
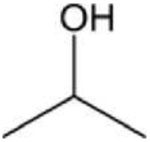
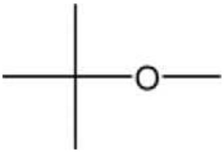
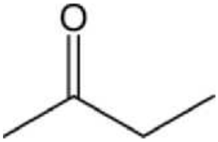
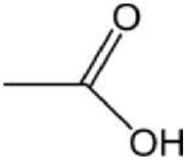
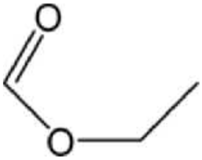
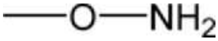
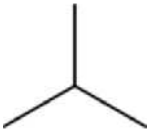
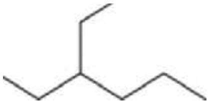


Figure 3.7. Methyl and methylamine. Popularized in the show Breaking Bad

A list of possible substituents is presented in Table 3.4, and then examples of their use are shown thereafter.

Table 3.4. Substituent nomenclature

Substituent	Name	Suffix or Prefix	Name Location	Example
F/Cl/Br/I	Fluoride/ chloride/ bromide/ iodide	Fluoride/ chloride/ bromide/ iodide	Before	 1,1,2-Trichloropropane
$-NH_2$	Amine	Amine	After	 Methylamine
$-OH$	Alcohol	~ol	After	 2-Propanol
$-O-$	Ether	Ether	After	 Methyl t-butyl ether

Substituent	Name	Suffix or Prefix	Name Location	Example
=O	Ketone	~one	After	 2-Butanone
COOH	Carboxylic acid	~oic acid	After	 Ethanoic acid
COOC	Ester	~oate	After	 Ethyl methanoate
CON	Amide	~amide	After	 Methanamide
CH_3	Methyl	Methyl	Before	 2-Methyl propane
C_2H_5	Ethyl	Ethyl	Before	 3-Ethyl hexane

3.2.4 BRANCHES

Often organic compounds will have multiple chains of carbon groups attached together, forming a branching structure as seen in Figure 3.8. In this case, the first task is to identify the longest chain of carbons. This will be the basis of the name for the compound.

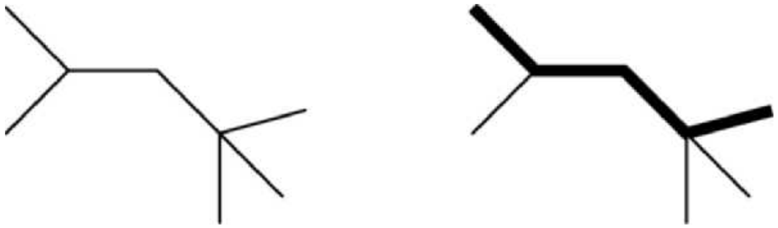


Figure 3.8. Branching organic compound. Names for these compounds are based on the longest carbon chain as shown on the right

Shown in Figure 3.8 is the compound with the trivial name isooctane. It forms part of the basis of octane ratings for gasoline. The longest straight chain of carbons found in this molecule is five carbons long, so its technical name would be rooted in pentane. There are three short side chains with one carbon each. One carbon side chains are "methyl" groups. The location of the side chains is indicated as before, with numbers indicating which carbon the substituents are on. Since lowest numbers are preferred, the two methyl groups on the same carbon would be numbered first. The name is 2,2,4-trimethylpentane.

3.3 AROMATIC COMPOUNDS

Aromatic compounds are a special subset of carbon compounds with a unique mode of bonding. The most commonly encountered aromatic compounds are the ones based on a six-member carbon ring, benzene, as shown in Figure 3.9.

In the depiction of benzene, the simplest aromatic compound, it is noted that there are three double bonds and three single bonds shown between the carbons. The three double bonds could be arranged to be between two different sets of carbons and retain the same general structure. In reality, neither structure is true, but rather all bonds in the molecule are about 1.5 bonds (strange as the nonintegral bond count may be). This effect is called resonance, and gives the molecule extra stability.

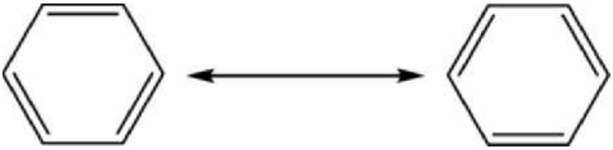


Figure 3.9. A benzene ring. This six-carbon ring is the basis of many common aromatic compounds

The rules for naming aromatic compounds are generally the same as for aliphatic compounds. The locations of substituents are identified with a number. If there are multiple options, the lowest possible numbers to be used is the preferred option. If different types of substituents exit, alphabetical order is preferred.

Example 3.2

Name the following aromatic compounds.

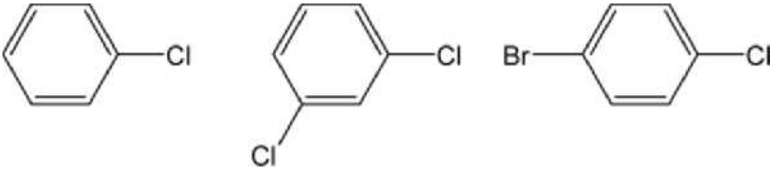


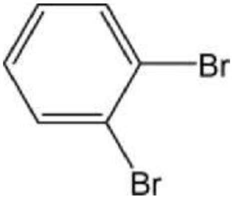
Figure 3.10. Aromatic substitutions

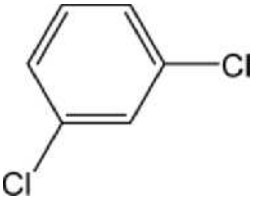
Solution

The first molecule shown in Figure 3.10 would be chlorobenzene. No distinction is necessary beyond that, as the chlorine could be on any of the carbons, and the molecule would still be the same. The second is 1,3-dichlorobenzene. The third is 1,4-bromochlorobenzene.

In some cases older nomenclature is used, with the words meta, para, and ortho indicating the locations of substituents. Table 3.5 lists the correlation between the different types of nomenclature.

Table 3.5. Substitution patterns in aromatic compounds

Name	Pattern	Use	Structure
ortho	1,2 substitution	*o*-Dibromobenzene	

Name	Pattern	Use	Structure
meta	1,3 substitution	*m*-Dichlorobenzene	
para	1,4 substitution	*p*-Dichlorobenzene	

Other substituents are also named as in the preceding cases for aliphatics.

3.4 ISOMERS AND CONGENERS

With the vast array of ways to arrange carbon atoms with respect to one another, sometimes the same chemical formula will give rise to an array of molecules that all have the same number and type of atoms, but with different structures, and therefore slightly or significantly different properties. These variations are called isomers.

Isomerization can be as simple as the rearrangement of substituents in a molecule. For an example, see the case of dichloropropane described earlier, Figure 3.3. There are four different ways to arrange two chlorine atoms on a propane backbone, leading to four different structural isomers of the compound.

A type of structural isomerization is observable for alkenes that can become important in plastics and polymers (see Section 3.5). Alkenes are different from alkanes in that rotation around a double bond is not possible, making the location of substituents on the two doubly bonded carbons distinct. If the substituents are on the same side of the double bond, the configuration is referred to as cis. If the substituents are on opposite sides, the configuration is trans. Figure 3.11 shows examples of cis and trans substitutions. These configurations can make a significant difference in chemical properties of materials made from the different isomers.

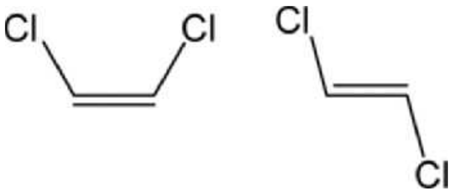


Figure 3.11. cis-Dichloroethene (left) and trans-dichloroethene (right)

A more drastic example would be that of C_2H_6O. There are two ways, as shown in Figure 3.12, that these atoms can be arranged into a compound, but unlike dichloropropane, their properties are very different, as seen in Table 3.6.

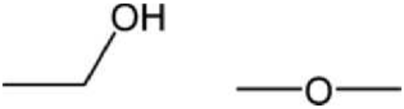


Figure 3.12. Two structure of C2H6O. Ethanol on the left, dimethyl ether on the right.

Table 3.6. Properties associated with structures in Figure 3.12

Name	Ethanol	Dimethyl Ether
Melting point	−114°C	−141°C
Boiling point	78.4°C	−24°C
Density (as liquid)	0.789 g/cm^3	0.735 g/cm^3
Solubility in water	Miscible	71 g/L
Physiological effect	Intoxicant	Weak depressant

These two molecules are ethanol and dimethyl ether. Their physical and chemical properties are quite distinct, even though they are structural isomers of each other.

A further grouping of compounds that are similar is the classification of congeners. This is a significantly broader and somewhat vaguer term than isomers. Congeners refer to molecules that have the same basic makeup, but vary in number or location of substituents. In organic chemistry, this usually refers to a molecule with a various number of same or similar substituents. As an example, chloroethane, dichloroethane, trichloroethane, and other enumerations of chloroethane would fall into a class of congeners.

3.5 ESSENTIALS OF POLYMER CHEMISTRY

Polymers are materials whose molecules are made up of many (poly~) small subunits (~mers). The most familiar of these are plastics, which are actually a broad variety of different compounds. Many natural materials are also polymers; for example, rubbers are polymers, and the main structural component of wood, cellulose, is also a polymer.

A couple of definitions are important when talking about polymer chemistry. The precursor compound for a polymer is referred to as a monomer. Monomers are the individual molecules which react to form the compound. Segmers are what monomers turn into once the polymer is formed. Oligomers are polymers that only have a smaller number of individual subunits, on the order of at most tens of segmers.

3.5.1 ADDITION POLYMERS

Addition polymers are a class of polymers in which bonds between doubly bonded carbons are formed to link together individual subunits. The consequence is either the loss or movement of the double bonds. The simplest case is that of polyethylene, a very common plastic. Polyethylene is a polymer of ethene (ethylene is a trivial name for ethene). Figure 3.13 depicts this transformation. Arrows indicate the movement of one of the bonds from a double bond into a new bond between the monomers

Figure 3.13. Addition polymerization

Here the double bond of an ethene molecule is reduced to a single bond, as it makes a connection to the next ethene molecule in line. This causes a chain reaction, as the new bond forces the next ethene molecule to lose its double bond, and form a bond to a third ethene. This chain reaction propagates until thousands of units of ethenes are bound into a chain.

Other commonly encountered plastics, such as polyvinylchloride (PVC) and polystyrene, are also formed by addition polymerizations. Both of these plastics have a subunit that can be seen as an ethene with a substituent replacing one of its hydrogens. For PVC, the substituent is chlorine, and for polystyrene, the substituent is a benzene ring (the technical term for this is a phenyl substitution). This concept is illustrated in Figures 3.14 and 3.15.

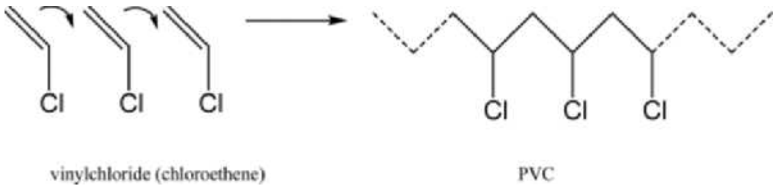


Figure 3.14. Formation of polyvinylchloride (PVC)

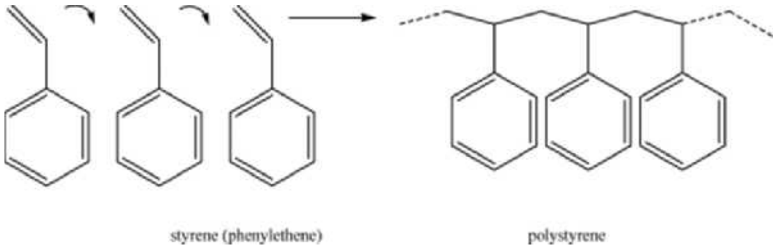


Figure 3.15. Formation of polystyrene

Rubbers are also formed from an addition polymerization, which is slightly more complex. The basic subunit here is an isoprene, which has two double bonds. The isoprene loses the double bonds at the two ends of the molecule, but gains one in the middle, for a net loss of one double bond and the formation of a polymer chain as shown in Figure 3.16.

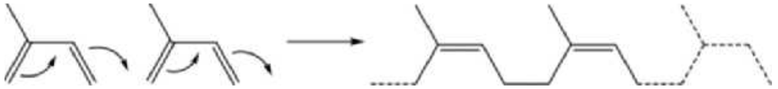


Figure 3.16. Complex addition polymerization in the formation of rubber

3.5.2 CONDENSATION POLYMERS

Another class of polymers is condensation polymers. As the name suggests, this type of polymerization generates water, or some others condensate, as a byproduct. Two common polymers formed by condensation are nylon, of which there are many varieties, and polycarbonates.

Nylon is formed from the reaction of a diamine and a dicarboxylic acid. The length of the carbon chain between the two amines and the two carboxylic acids will govern the mechanical properties of the polymer produced. Nylon is usually named as nylon-x,y; where x is the number of carbon atoms in the diamine compound and y is the number of carbon atoms in the dicarboxylic acid. The schematic for the synthesis of nylon 6,10 is shown in Figure 3.17.

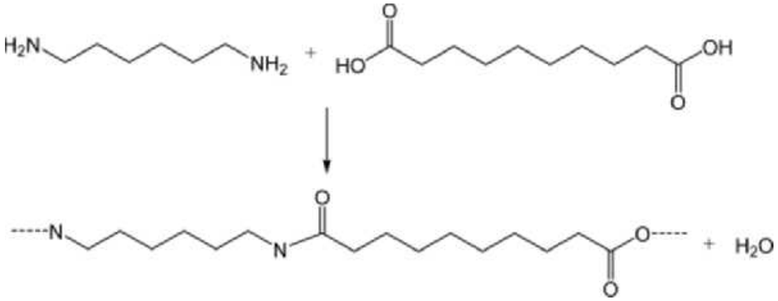


Figure 3.17. Condensation polymerization of nylon

Another important commodity chemical is polycarbonate. Polycarbonates are plastics that are hard, and also clear, and thus can be used as a substitute for glass in certain applications. The most common polycarbonate is made from bisphenol A and phosgene. The reaction shown in Figure 3.18 produces HCl as a condensate instead of H_2O, but the principle is the same.

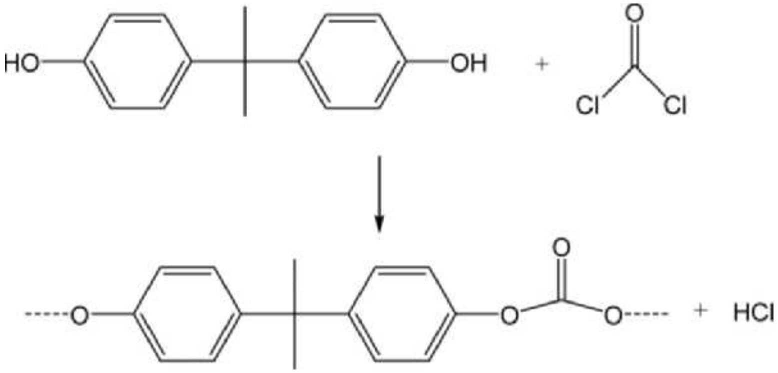


Figure 3.18. Condensation polymerization to form polycarbonates

3.5.3 COMMON POLYMERS

In Table 3.7, some common polymers and their structures are listed. They are also identified by their recycling code, which can often be found on plastic products.

Of note are HDPE and LDPE, which are very common plastics coded differently, but chemically apparently identical. HDPE and LDPE are made of the same monomer, but their larger scale structures are different. HDPE has very straight chains of polyethylene, and these stack on each other neatly to make a harder, denser, higher melting-point plastic. Polyethylene in LDPE tends to have branches, and this leads to the strands stacking relatively poorly. This makes LDPE softer, less dense, and lower melting relative to HDPE.

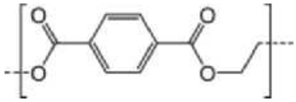
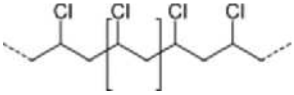
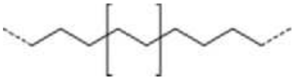
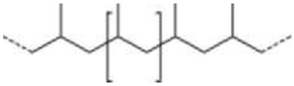
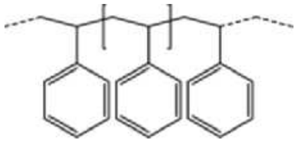
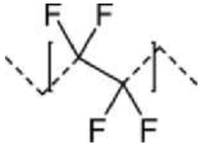
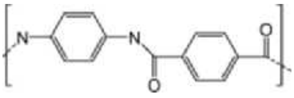
3.5.4 POLYMER CONCERNS

A major concern surrounding polymers is the potential for environmental contamination from use of plastics. This can occur either from leeching of unreacted monomers into the environment from the plastic, or from the breakdown of the plastic from years of exposure to UV light from the sun or other environmental conditions.

For instance, a major controversy surrounds the use of polycarbonate plastics in drinking bottles. When a polymerization reaction occurs, not all of the monomers react, and some end up trapped in the plastic, unreacted. One of the monomers, bisphenol A, was shown to have a biological effect, as it mimics the functions of certain hormones in the body. This could potentially affect the health of people who used the water bottles, as, over time, small amounts of the bisphenol A would leech into the water, and would end up being consumed by the owner. Alternative plastics with different feedstocks had to be developed to bypass this problem.

PVC faces similar potential concerns. Polyvinylchloride itself is a carcinogen, and if burned releases caustic HCl gas. Furthermore, as PVC ages, it has the potential to enter the biosphere as a potentially toxic microplastic. These concerns often lead to regulation, and have to be carefully considered when using or disposing of PVC.

Table 3.7. Common polymers

Name	Code	Structure	Example Uses
Polyethylene terephthalate (PETE)	1 PETE		Soda bottles, sails, polyester
High-density polyethylene (HDPE)	2 HDPE		Grocery bags, milk jugs, plastic lumber
Polyvinyl chloride (PVC or V)	3 V		Pipes, shower curtains, cleaning agent bottles
Low-density polyethylene (LDPE)	4 LDPE		Plastic bags, 6-pack rings, tubing
Polypropylene (PP)	5 PP		Ropes, packaging materials, food containers
Polystyrene (PS)	6 PS		Insulation, plastic utensils
polytetrafluoroethylene (Teflon)	* 7 OTHER		Cookware, low friction surfaces
Kevlar	* 7 OTHER		Body armor

Note: Brackets denote the segmers of the shown polymer.

*Code 7 classification is for "other" polymers, anything that does not fall into the other categories. Some examples of other polymers are given.

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