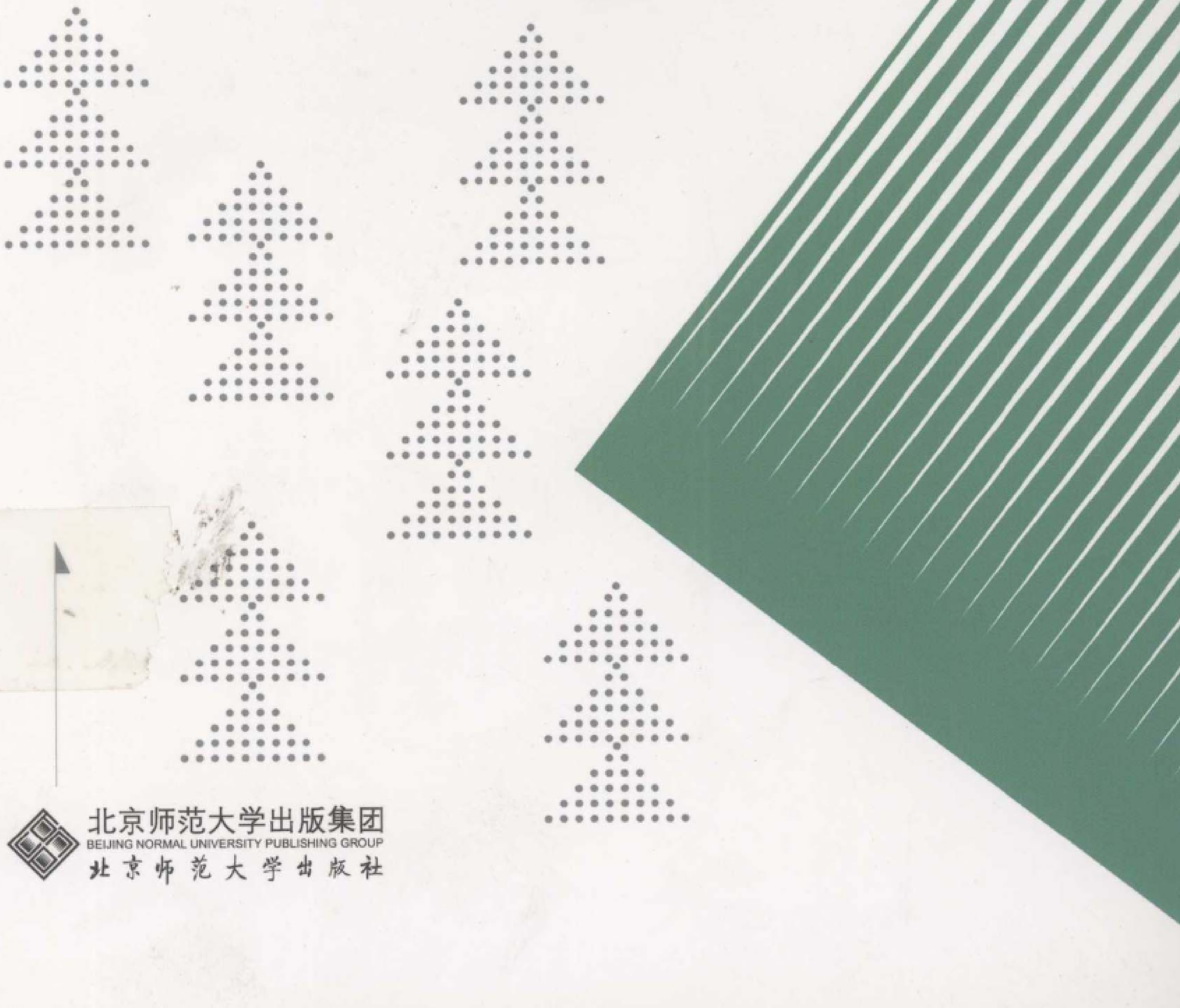
新世纪高等学校教材

化学系列教材

HUAXUE ZHUANYE

化学专业英语

汪辉亮　主　编



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前言

语言是思维和交流的工具。汉语无疑是世界上使用人口最多的语言，也是最古老、最优秀的语言之一。但另一个不得不承认的事实是，英语是当今世界上使用最广泛、影响力最大的语言。英语也是目前国际学术界进行交流的最重要的语言。对化学工作者而言，英语尤为重要，阅读文献、参加学术会议和发表论文等都离不开英语。

化学专业英语是各级各类高等院校化学专业学生的必修或选修课程。在教学过程中我们发现，有的学生即便修过一些双语化学课程，但对化学专业英语中一些基本的、简单的表达也不是很清楚。因此，我们认为，对学生进行系统的化学专业英语的训练是很有必要的。化学专业英语不同于普通英语之处在于其专业性，因此其重点为使学生掌握化学专业的基本词汇、术语和相关的表达方式，提高学生化学专业方面的英语能力。

本书共分9章，1～8章内容涉及了大学化学所涵盖的五个二级学科：无机化学、有机化学、分析化学、物理化学(含结构化学)、高分子化学，其中包括了元素、无机物、有机物和高分子的命名等，第9章为新材料。附录为实验室常用仪器和装置。本书在编写过程中参考了大量的相关各学科的英文原版教科书和期刊文章，同时还参考了很多网络资料。我们力求在本教材中将大学化学所涉及的化学专业词汇和表达都涵盖到。虽然化学专业英语的目的不是教给学生相关化学学科的专业知识，但我们在各章内容的选择上尽可能做到系统化、条理化。

本书由北京师范大学汪辉亮主编，河北师范大学于海涛、华南师范大学舒东、四川师范大学潘睿、北京师范大学王力元、河南师范大学赵扬和李慧珍等老师参与了部分章节的编写。

本书可用作综合性大学、师范大学及其他本科院校化学、化工专业的本科生及研究生的专业英语教材，也可用作与化学相关人员的参考资料。

由于编写时间有限，在本书中没有注释和练习题。同时，由于编者水平的限制，书中难免存在错误和不当之处，敬请读者指正。

最后对各位作者对本书作出的贡献表示衷心感谢。

编　者
2010年9月

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Chapter 1 Matter and Measurement

Chemistry is the science of matter and the changes it undergoes. Chemists study the composition, structure, and properties of matter. They observe the changes that matter undergoes and measure the energy that is produced or consumed during these changes. Chemistry provides an understanding of many natural events and has led to the synthesis of new forms of matter that have greatly affected the way we live.

Disciplines within chemistry are traditionally grouped by the type of matter being studied or the kind of study. These include **inorganic chemistry**, **organic chemistry**, **physical chemistry**, **analytical chemistry**, **polymer chemistry**, **biochemistry**, and many more specialized disciplines, e. g. **radiochemistry**, **theoretical chemistry**.

Chemistry is often called "**the central science**" because it connects the other natural sciences such as astronomy, physics, material science, biology and geology.

1.1 Classification of Matter

Matter is usually defined as anything that has mass and occupies space. **Mass** is the amount of matter in an object. The mass of an object does not change. The **volume** of an object is how much space the object takes up.

All the different forms of matter in our world fall into two principal categories: (1) pure substances; (2) mixtures. A **pure substance** can also be defined as a form of matter that has both definite composition and distinct properties. Pure substances are subdivided into two groups: elements and compounds. An **element** is the simplest kind of material with unique physical and chemical properties; it can not be broken down into anything simpler by either physical or chemical means. A **compound** is a pure substance that consists of two or more elements linked together in characteristic and definite proportions; it can be decomposed by a chemical change into simpler substances with a fixed mass ratio. **Mixtures** contain two or more chemical substances in variable proportions in which the pure substances retain their chemical identities. In principle, they can be separated into the component substances by physical means, involving physical changes. A sample is **homogeneous** if it always has the same composition, no matter what part of the sample is examined. Pure elements and pure chemical compounds are homogeneous. Mixtures can be homogeneous, too; in a **homogeneous mixture** the constituents are distributed uniformly and the composition and appearance of the mixture are uniform throughout. A **solutions** is a special type of homogeneous mixture. A **heterogeneous mixture** has physically distinct parts with different properties. The classification of matter is summarized in the diagram below:

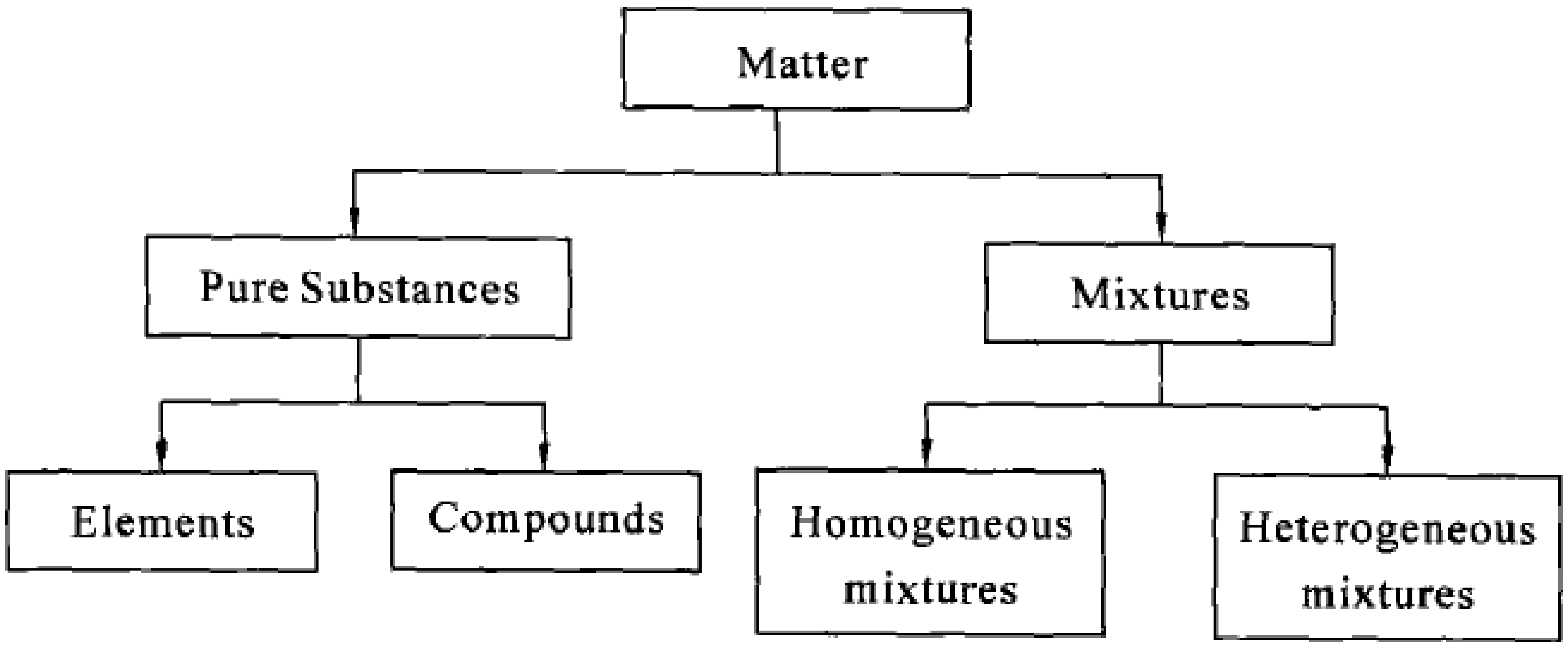


Figure 1.1 Classification of Matter

Matter can also be categorized into four distinct phases: solid, liquid, gas, and plasma. The **solid** phase of matter has the atoms packed closely together. An object that is solid has a definite shape and volume that cannot be changed easily. The **liquid** phase of matter has the atoms packed closely together, but they flow freely around each other. Matter that is liquid has a definite volume but changes shape quite easily. Solids and liquids are termed *condensed phases* because of their well-defined volumes. The **gas** phase of matter has the atoms loosely arranged so they can travel in and out easily. A gas has neither specific shape nor constant volume. The **plasma** phase of matter has the atoms existing in an **excited** state.

1.2 Properties of Matter

All substances have properties, the characteristics that give each substance its unique identity. We learn about matter by observing its properties. To identify a substance, chemists observe two distinct types of properties, physical and chemical, which are closely related to two types of change that matter undergoes.

Physical properties are those that a substance shows by itself, without changing into or interacting with another substance. Some physical properties are color, smell, temperature, boiling point, electrical conductivity, and density. A **physical change** is a change that does not alter the chemical identity of the matter. A physical change results in different physical properties. For example, when ice melts, several physical properties have changed, such as hardness, density, and ability to flow. But the sample has not changed its composition: it is still water.

Chemical properties are those that do change the chemical nature of matter. A **chemical change**, also called a chemical reaction, is a change that does alter the chemical identity of the substance. It occurs when a substance (or substances) is converted into a different substance (or substances). For example, when hydrogen burns in air, it undergoes a chemical change because it combines with oxygen to form water.

Separation of Mixtures

The separation of mixtures into its constituents in a pure state is an important process in chemistry. The constituents of any mixture can be separated on the basis of their differences in their physical and chemical properties e.g. particle size, solubility, effect of heat, acidity or basicity etc.

Some of the methods for separation of mixtures are:

(1)Sedimentation or decantation. To separate the mixture of coarse particles of a solid from a liquid e.g. muddy river water.

(2) Filtration. To separate the insoluble solid component of a mixture from the liquid completely i.e. separating the precipitate (solid phase) from any solution.

(3)Evaporation. To separate a non-volatile soluble salt from a liquid or recover the soluble solid solute from the solution.

(4)Crystallization. To separate a solid compound in pure and geometrical form.

(5)Sublimation. To separate volatile solids, from a non-volatile solid.

(6)Distillation. To separate the constituents of a liquid mixture, which differ in their boiling points.

(7) Solvent extraction method. Organic compounds, which are easily soluble in organic solvents but insoluble or immiscible with water forming two separate layers can be easily separated.

1.3 Atoms, Molecules and Compounds

The fundamental unit of a chemical substance is called an **atom**. The word is derived from the Greek *atomos*, meaning "undivisible" or "uncuttable". An atom is the smallest possible particle of a substance.

Molecule is the smallest particle of a substance that retains the chemical and physical properties of the substance and is composed of two or more atoms; a group of like or different atoms held together by chemical forces. A molecule may consist of atoms of a single chemical element, as with oxygen (O_2), or of different elements, as with water (H_2O).

A **chemical element** is a pure chemical substance consisting of one type of atom distinguished by its **atomic number**, which is the number of protons in its nucleus. The term is also used to refer to a pure chemical substance composed of atoms with the same number of protons. Until March 2010, 118 elements have been observed. 94 elements occur naturally on earth, either as the pure element or more commonly as a component in compounds. 80 elements have stable isotopes, namely all elements with atomic numbers 1 to 82, except elements 43 and 61 (*technetium* and *promethium*). Elements with atomic numbers 83 or higher (*bismuth* and above) are inherently unstable, and undergo *radioactive decay*. The elements from atomic number 83 to 94 have no stable nuclei, but are nevertheless found in nature, either surviving as remnants of the primordial stellar *nucleosynthesis* that produced the elements in the solar system, or else produced as short-lived daughter-isotopes through the natural decay of uranium and thorium. The remaining 24 elements are *artificial* or *synthetic* elements, which are products of man-induced processes. These synthetic elements are all characteristically unstable. Although they have not been found in nature, it is conceivable that in the early history of the earth, these and possibly other unknown elements may have been present. Their unstable nature could have resulted in their disappearance from the natural components of the earth, however.

The naturally occurring elements were not all discovered at the same time. Some, such as *gold*, *silver*, *iron*, *lead*, and *copper*, have been known since the days of earliest civilizations. Others, such as *helium*, *radium*, *aluminium*, and *bromine*, were discovered in the nineteenth century. The most abundant elements found in the earth's crust, in order of decreasing percentage, are *oxygen*, *silicon*, *aluminium*, and *iron*. Others present in amounts of 1% or more are *calcium*, *sodium*, *potassium*, and *magnesium*. Together, these represent about 98.5% of the earth's crust.

The nomenclature and their origins of all known elements will be described in Chapter 2.

A **chemical compound** is a pure chemical substance consisting of two or more different chemical elements that can be separated into simpler substances by chemical reactions. Chemical compounds have a unique and defined chemical structure; they consist of a fixed ratio of atoms that are held together in a defined spatial arrangement by *chemical bonds*. Compounds that exist as molecules are called **molecular compounds**. An **ionic compound** is a chemical compound in which ions are held together in a lattice structure by *ionic bonds*. Usually, the positively charged portion consists of metal **cations** and the negatively charged portion is an **anion** or *polyatomic ion*.

The relative amounts of the elements in a particular compound do not change: Every molecule of a particular chemical substance contains a characteristic number of atoms of its constituent elements. For example, every water molecule contains two hydrogen atoms and one oxygen atom. To describe this atomic composition, chemists write the **chemical formula** for water as H_2O.

The chemical formula for water shows how formulas are constructed.

The formula lists the symbols of all elements found in the compound, in this case H (hydrogen) and O (oxygen). A subscript number after an element's symbol denotes how many atoms of that element are present in the molecule. The subscript 2 in the formula for water indicates that each molecule contains two hydrogen atoms. No subscript is used when only one atom is present, as is the case for the oxygen atom in a water molecule. Atoms are indivisible, so molecules always contain whole numbers of atoms. Consequently, the subscripts in chemical formulas of molecular substances are always integers. We explore chemical formulas in greater detail in Chapter 2.

The simple formula that gives the simplest whole number ratio between the atoms of the various elements present in the compound is called its **empirical formula**. The simplest formula that gives the actual number of atoms of the various elements present in a molecule of any compound is called its **molecular formula**. **Elemental analysis** is an experiment that determines the amount (typically a weight percent) of an element in a compound. The elemental analysis permits determination of the empirical formula, and the molecular weight and elemental analysis permit determination of the molecular formula.

1.4 Numbers in Physical Quantities

1.4.1 Measurement

1. Physical Quantities

Physical properties such as *height*, *volume*, and *temperature* that can be measured are called **physical quantity**. A number and a unit of defined size are required to describe physical quantity, for example, 10 meters, 9 kilograms.

2. Exact Numbers

Exact Numbers are numbers known with certainty. They have unlimited number of significant figures. They arise by directly counting numbers, for example, the number of sides on a square, or by definition:

$$1\ \text{m} = 100\ \text{cm},\ 1\ \text{kg} = 1000\ \text{g}$$

$$1\ \text{L} = 1000\ \text{mL},\ 1\ \text{minute} = 60\ \text{seconds}$$

3. Uncertainty in Measurement

Numbers that result from measurements are *never* exact. Every experimental measurement, no matter how precise, has a degree of uncertainty to it because there is a limit to the number of digits that can be determined. There is always some degree of uncertainty due to experimental errors: limitations of the measuring instrument, variations in how each individual makes measurements, or other conditions of the experiment.

4. Precision and Accuracy

In the fields of engineering, industry and statistics, the **accuracy** of a measurement system is the degree of *closeness* of measurements results to its *actual* (*true*) value. The **precision** of a measurement system, also called *reproducibility* or *repeatability*, is the degree to which repeated measurements under unchanged conditions show the same results. Although the two words can be synonymous in colloquial use, they are deliberately contrasted in the context of the scientific method.

A measurement system can be accurate but not precise, precise but not accurate, neither, or both. A measurement system is called *valid* if it is both accurate and precise. Related terms are **bias** (non-random or directed effects caused by a factor or factors unrelated by the independent variable) and **error** (random variability), respectively. **Random errors** result from uncontrolled variables in an experiment and affect precision; **systematic errors** can be assigned to definite causes and affect accuracy. For example, if an experiment contains a systematic error, then increasing the sample size generally increases precision but does not improve accuracy. Eliminating the systematic error improves accuracy but does not change precision.

1.4.2 Significant Figures

The number of digits reported in a measurement reflects the accuracy of the measurement and the precision of the measuring device. **Significant figures** in a number include all of the digits that are known with certainty, plus the first digit to the right that has an uncertain value. For example, the uncertainty in the mass of a powder sample, e.g. 3.1267g as read from an "analytical balance" is ±0.0001g.

In any calculation, the results are reported to the fewest significant figures (for multiplication and division) or fewest decimal places (addition and subtraction).

1. Rules for deciding the number of significant figures in a measured quantity

The number of significant figures is found by counting from left to right, beginning with the first nonzero digit and ending with the digit that has the uncertain value, e.g.

459 (3) 0.206 (3) 2.17(3) 0.00693 (3) 25.6 (3) 7390 (3) 7390. (4)

(1) All nonzero digits are significant, e.g. 1.234 g has 4 significant figures, 1.2 g has 2 significant figures.

(2) Zeroes between nonzero digits are significant: e.g. 1,002 kg has 4 significant figures, 3.07 mL has 3 significant figures.

(3) Leading zeroes to the left of the first nonzero digits are not significant; such zeroes merely indicate the position of the decimal point: e.g. 0.001 m has only 1 significant figure, 0.012 g has 2 significant figures.

(4) Trailing zeroes that are also to the right of a decimal point in a number are significant: e.g. 0.0230 mL has 3 significant figures, 0.20 g has 2 significant figures.

(5) When a number ends in zeroes that are not to the right of a decimal point, the zeroes are not necessarily significant: e.g. 190 miles may be 2 or 3 significant figures, 50,600 calories may be 3, 4, or 5 significant figures.

The potential ambiguity in the last rule can be avoided by the use of *standard exponential*, or *"scientific" notation*. For example, depending on whether the number of significant figures is 3, 4, or 5, we would write 50,600 calories as:

5.06×10^4 calories (3 significant figures),

5.060×10^4 calories (4 significant figures), or

5.0600×10^4 calories (5 significant figures).

2. Rules for rounding off numbers

(1) If the digit to be dropped is greater than 5, the last retained digit is increased by one. For example, 12.6 is rounded to 13.

(2)If the digit to be dropped is less than 5, the last remaining digit is left as it is. For example, 12.4 is rounded to 12.

(3)If the digit to be dropped is 5, and if any digit following it is not zero, the last remaining digit is increased by one. For example, 12.51 is rounded to 13.

(4)If the digit to be dropped is 5 and is followed only by zeroes, the last remaining digit is increased by one if it is odd, but left as it is if even. For example, 11.5 is rounded to 12, 12.5 is rounded to 12.

This rule means that if the digit to be dropped is 5 followed only by zeroes, the result is always rounded to the even digit. The rationale is to avoid bias in rounding: half of the time we round up, half the time we round down.

3. Arithmetic using significant figures

In carrying out calculations, the general rule is that the accuracy of a calculated result is limited by the least accurate measurement involved in the calculation.

(1) In *addition* and *subtraction*, the result is rounded off to the last common digit occurring furthest to the right in all components. Another way to state this rules, is that, in addition and subtraction, the result is rounded off so that it has the same number of decimal places as the measurement having the fewest decimal places. For example,

100 (assume 3 significant figures) + 23.643 (5 significant figures) = 123.643

which should be rounded to 124 (3 significant figures).

(2) In *multiplication* and *division*, the result should be rounded off so as to have the same number of significant figures as in the component with the least number of significant figures. For example,

3.0 (2 significant figures) × 12.60 (4 significant figures) = 37.8000

which should be rounded off to 38 (2 significant figures).

1.4.3 Scientific Notation

Scientific notation, also known as **standard form** or as **exponential notation**, is a way of writing numbers that accommodates values too large or small to be conveniently written in standard decimal notation.

In scientific notation, all numbers are written like this:

$$a \times 10^{b}$$

(a times ten to the power of b), where the *exponent* b is an integer, and the *coefficient* a is any real number, called the *significant* or *mantissa* (though the term "mantissa" may cause confusion as it can also refer to the fractional part of the common logarithm). If the number is negative then a *minus sign* precedes a (as in ordinary decimal notation).

In standard scientific notation the significant figures of a number are retained in a factor between 1 and 10 and the location of the decimal point is indicated by a power of 10. For example:

An electron's mass is about 0.00000000000000000000000000000091093822 kg. In scientific notation, this is written $9.1093822 \times 10^{-31}$ kg. The Earth's mass is about 5973600000000000000000000 kg. In scientific notation, this is written 5.9736×10^{24} kg.

1.5 Units of Measurement

1.5.1 Systems of Measurement

1. United States Customary System (USCS)

The United States Customary System (also called American system) is the most commonly used system of measurement in the United States. It is similar but not identical to the *British Imperial units*. The U.S. is the only industrialized nation that does not mainly use the metric system in its commercial and standards activities. Base units are defined but seem arbitrary (e.g. there are 12 inches in 1 foot).

2. Metric

The metric system is an international *decimalized* system of measurement, first adopted by France in 1791, that is the common system of measuring units used by most of the world. It exists in several variations, with different choices of fundamental units, though the choice of base units does not affect its day-to-day use. Over the last two centuries, different variants have been considered the metric system. Metric units are universally used in scientific work, and widely used around the world for personal and commercial purposes. A standard set of prefixes in powers of ten may be used to derive larger and smaller units from the base units.

3. SI

SI system (for Système International) was adopted by the International Bureau of Weights and Measures in 1960, it is a revision and extension of the metric system. Scientists and engineers throughout the world in all disciplines are now being urged to use only the SI system of units.

1.5.2 SI base units

The SI is founded on seven SI *base units* for seven *base quantities* assumed to be mutually independent, as given in Table 1.1.

Table 1.1 SI Base Physical Quantities and Units

Unit Name	Unit Symbol	Base Quantity	Quantity Symbol	Dimension Symbol
meter	m	length	l	**L**
kilogram	kg	mass	m	**M**
second	s	time	t	**T**
ampere	A	electric current	I	**I**
kelvin	K	thermodynamic temperature	T	**Θ**
mole	mol	amount of substance	n	**N**
candela	cd	luminous intensity	I_v	**J**

1.5.3 SI derived units

Other quantities, called *derived quantities*, are defined in terms of the seven base quantities via a system of quantity equations. The SI derived units for these derived quantities are obtained from these equations and the seven SI base units. Examples of such SI derived units are given in Table 1.2, where it should be noted that the symbol 1 for quantities of dimension 1 such as mass fraction is generally omitted.

Table 1.2 SI Derived Physical Quantities and Units

Quantity (symbol)	Name of Unit (symbol)	Derived Unit
area (A)	square meter	m^2
volume (V)	cubic meter	m^3
density (ρ)	kilogram per cubic meter	$kg \cdot m^{-3}$
velocity (u)	meter per second	$m \cdot s^{-1}$
pressure (p)	pascal (Pa)	$kg \cdot m^{-1} \cdot s^{-2}$
energy (E)	joule (J)	$kg \cdot m^2 \cdot s^{-2}$
frequency (ν)	hertz (Hz)	s^{-1}
quantity of electricity (Q)	coulomb (C)	$A \cdot s$
electromotive force (E)	volt (V)	$kg \cdot m^2 \cdot A^{-1} \cdot s^{-3}$
force (F)	newton (N)	$kg \cdot m \cdot s^{-2}$

For ease of understanding and convenience, 22 SI derived units have been given special names and symbols, as shown in Table 1.3.

Table 1.3 SI Derived Units with special names and symbols

Derived quantity	Special name	Special Symbol	Expression in terms of	
			other SI units	SI base units
plane angle	radian	rad		$m \cdot m^{-1} = 1$
solid angle	steradian	sr		$m^2 \cdot m^{-2} = 1$
frequency	hertz	Hz		s^{-1}
force	newton	N		$m \cdot kg \cdot s^{-2}$
pressure, stress	pascal	Pa	$N \cdot m^{-2}$	$m^{-1} \cdot kg \cdot s^{-2}$
energy, work, quantity of heat	joule	J	$N \cdot m$	$m^2 \cdot kg \cdot s^{-2}$
power, radiant flux	watt	W	$J \cdot s^{-1}$	$m^2 \cdot kg \cdot s^{-3}$
electric charge quantity of electricity	coulomb	C		$s \cdot A$
electric potential, potential difference, electromotive force	volt	V	$W \cdot A^{-1}$	$m^2 \cdot kg \cdot s^{-3} \cdot A^{-1}$

Continued

Derived quantity	Special name	Special symbol	Expression in terms of	
			other SI units	SI base units
capacitance	farad	F	$C \cdot V^{-1}$	$m^{-2} \cdot kg^{-1} \cdot s^4 \cdot A^2$
electric resistance	ohm	Ω	$V \cdot A^{-1}$	$m^2 \cdot kg \cdot s^{-3} \cdot A^{-2}$
electric conductance	siemens	S	$A \cdot V^{-1}$	$m^{-2} \cdot kg^{-1} \cdot s^2 \cdot A^2$
magnetic flux	weber	Wb	$V \cdot s$	$m^2 \cdot kg \cdot s^{-2} \cdot A^{-1}$
magnetic flux density	tesla	T	$Wb \cdot m^{-2}$	$kg \cdot s^{-2} \cdot A^{-1}$
inductance	henry	H	$Wb \cdot A^{-1}$	$m^2 \cdot kg \cdot s^{-2} \cdot A^{-2}$
Celsius temperature	degree Celsius	°C		K
luminous flux	lumen	lm	$cd \cdot sr$	$cd \cdot sr$
illuminance	lux	lx	$lm \cdot m^{-2}$	$m^{-2} \cdot cd \cdot sr$
activity (of a radionuclide)	becquerel	Bq		s^{-1}
absorbed dose, specific energy (imparted), kerma	gray	Gy	$J \cdot kg^{-1}$	$m^2 \cdot s^{-2}$
dose equivalent, *et al.*	sievert	Sv	$J \cdot kg^{-1}$	$m^2 \cdot s^{-2}$
catalytic activity	katal	kat		$s^{-1} \cdot mol$

Certain units that are not part of the SI are essential and used so widely that they are accepted by the CIPM (Commission International des Poids Et Mesures) for use with the SI. Some commonly used units are given in Table 1.4.

Table 1.4 Non-SI units accepted for use with the SI

Name	Symbol	Quantity	Equivalent SI unit
minute	min	time	1 min = 60 s
hour	h	time	1 h = 60 min = 3600 s
day	d	time	1 d = 24 h = 1440 min = 86400 s
degree of arc	°	plane angle	$1^\circ = \left(\frac{\pi}{180}\right)$ rad

Continued

Name	Symbol	Quantity	Equivalent SI unit
minute of arc	′	plane angle	$1' = \left(\frac{1}{60}\right)^{\circ} = \left(\frac{\pi}{10800}\right)$ rad
second of arc	″	plane angle	$1'' = \left(\frac{1}{60}\right)' = \left(\frac{1}{3600}\right)^{\circ} = \left(\frac{\pi}{648000}\right)$ rad
hectare	ha	area	$1\ \text{ha} = 100\ \text{a} = 10000\ \text{m}^2$
litre	l or L	volume	$1\ \text{L} = 1\ \text{dm}^3 = 0.001\ \text{m}^3$
tonne	t	mass	$1\ \text{t} = 10^3\ \text{kg} = 1\ \text{Mg}$

The 20 SI prefixes used to form decimal multiples and submultiples of SI units are given in Table 1.5.

Table 1.5 SI Prefixes

Factor	Name	Symbol	Factor	Name	Symbol
10^{24}	yotta	Y	10^{-1}	deci	d
10^{21}	zetta	Z	10^{-2}	centi	c
10^{18}	exa	E	10^{-3}	milli	m
10^{15}	peta	P	10^{-6}	micro	μ
10^{12}	tera	T	10^{-9}	nano	n
10^{9}	giga	G	10^{-12}	pico	p
10^{6}	mega	M	10^{-15}	femto	f
10^{3}	kilo	k	10^{-18}	atto	a
10^{2}	hecto	h	10^{-21}	zepto	z
10^{1}	deka	da	10^{-24}	yocto	y

1.5.4 Units of Measurement in Chemistry

1. Mass

Mass is defined as the amount of matter in an object. The standard SI unit of mass is the kilogram (1 kg weighs 2.205 lb). Smaller mass units are frequently used in chemistry.

$$1\ \text{gram} = 0.001\ \text{kg} = 1.0 \times 10^{-3}\ \text{kg}$$

$$1\ \text{milligram}\ (1\ \text{mg}) = 1.0 \times 10^{-3}\ \text{g}$$

$$1\ \text{microgram}\ (1\mu\text{g}) = 1.0 \times 10^{-6}\ \text{g}$$

Note that the terms *mass* and *weight* are used interchangeably, but they do have different meanings. **Mass** is the amount of matter in an object, while **weight** is a measure of the pull of gravity on an object. Strictly speaking, weight should be expressed in units of force. In practice, however, the distinction between weight and mass is often ignored. Expressions such as "weigh out 30 grams of this material," or "How many grams does that sample weigh?" are often used.

2. Length

Meter (m) is the standard measure of length or distance in both SI and metric system. Centimeter (cm; 10^{-2} m) and millimeter (mm; 10^{-3} m) are commonly used for most measurements in chemistry and medicine.

$$1\ \text{Å} = 10^{-10}\ \text{m} = 0.1\ \text{nm}$$

3. Volume

Volume is the amount of space occupied by an object. The SI unit for volume is the cubic meter (m^3). Liter (L) is commonly used in chemistry as a unit of volume. 1 L = 0.001 m^3 = 1 dm^3. One liter has the volume a cube 10 cm (1 dm) on edge. One liter is further divided into 1000 milliliters (mL). 1 mL has the volume of a cube with 1 cm on edge. 1 milliliter is often called 1 cubic centimeter (1 mL = 1 cm^3).

4. Density

Density relates the mass of an object with its volume. Density is usually expressed in units as Gram per cubic centimeter ($g \cdot cm^{-3}$) for solids, and Gram per milliliter ($g \cdot mL^{-1}$) for liquids.

$$\text{Density} = \frac{\text{mass (g)}}{\text{volume (cm}^3\text{)}}$$

5. Temperature

Temperature is the measure of how hot or cold an object is. There are three temperature scales: the SI scale, measured in Kelvin units (K); the Celsius or centigrade scale, measured in degrees Celsius (°C); and the Fahrenheit scale, measured in degrees Fahrenheit (°F).

$$℃ = \left[(℉ + 40) \left(\frac{5}{9} \right) \right] - 40$$

$$℉ = \left[(℃ + 40) \left(\frac{9}{5} \right) \right] - 40$$

$$K = ℃ + 273.15$$

6. Energy and Heat

Energy is the capacity to do work or supply energy. Energy can be classified into ***Potential Energy*** (stored energy) and ***Kinetic Energy*** (energy of motion).

In chemical reactions, the *potential energy* is often converted into *heat*. Reaction products have less potential energy than the reactants — the products are more *stable* than the reactants. Stable products have very little potential energy remaining as a result have very little tendency to undergo further reaction. SI unit of energy is Joule (J) and the metric unit of energy is calorie (cal).

1 cal (calorie) = 4. 184 J

Heat is the energy transferred from a hot object to a cold one when the two are in contact. The amount of heat needed to raise the temperature of 1 g of a substance by 1℃ is called the ***Specific Heat*** of the substance. Unit of specific heat is $\text{cal} \cdot \text{g}^{-1} \cdot ℃^{-1}$.

It is possible to calculate how much heat must be added or removed to accomplish a given temperature change of a given mass of a substance.

7. Force and Pressure

In physics, a force is any influence that causes a free body to undergo an acceleration. The SI unit of force is the newton (symbol N), which is the force required to accelerate a one kilogram mass at a rate of one meter per second squared, or $kg \cdot m \cdot s^{-2}$.

$$1\ N = 1\ kg \cdot m \cdot s^{-2}$$

$$1\ Pa = 1\ N \cdot m^{-2} = 1\ kg \cdot m^{-1} \cdot s^{-2}$$

Pressure is the force per unit area applied in a direction perpendicular to the surface of an object. The SI unit for pressure is the pascal (Pa), equal to one newton per square meter ($N \cdot m^{-2}$ or $kg \cdot m^{-1} \cdot s^{-2}$). The non-SI units for pressure include atmospheres (atm), bars (bar), pounds per square inch (psi), torr (Torr), and millimeters of mercury (mmHg).

1.6 The Dimensional Method

The numerical value of a measurement should always be expressed together with the correct unit. Converting from one dimensional unit to another is often somewhat complex and being able to perform such conversions is an important skill to acquire.

The **factor-label method**, also known as the *unit-factor method* or *dimensional analysis*, is a widely used approach for performing such conversions. A quantity in one unit is converted to an equivalent quantity in a different unit by using a *conversion factor* derived from the numerical relationship between the two units.

A **conversion factor** is a numerical factor used to multiply or divide a quantity when converting from one system of units to another. All conversion factors are equal to 1 because the value of the *numerator* and the *denominator* are equal. Thus, using a conversion factor in a calculation is equivalent to multiplying by 1. In a calculation, conversion factors are manipulated so that the units cancel out, leaving a number in the desired new units. Conversion factors or physical constants should include a sufficient number of significant figures so as not to affect the uncertainty of the answer. (If a conversion factor is an exact number it can be treated as having as many significant figures as needed.)

For example, convert 50.0 mL to liters:

$$50.0\ mL \times \frac{1\ L}{1000\ mL} = 0.0500\ L\ \text{(3 significant figures)}$$

In a problem, units are multiplied, divided, and cancelled exactly as numbers would be. If the problem is correctly set up and worked, it should produce an answer in the correct units. For example,

$$9.0\ \mathrm{m} + 3.29\ \mathrm{m} = 12.3\ \mathrm{m}$$

$$635\mathrm{N} - 91\ \mathrm{N} = 544\ \mathrm{N}$$

$$(16.0\ \mathrm{A})^2 = 256\ \mathrm{A}^2$$

$$\frac{4.0\ \mathrm{cm}}{2.0\ \mathrm{s}} = 2.0\ \mathrm{cm/s} = 2.0\ \mathrm{cm} \cdot \mathrm{s}^{-1}$$

$$\frac{210\ \mathrm{kcal}}{69\ \mathrm{kcal}} = 3.0$$

$$1.2\ \mathrm{eV} \cdot \frac{1.6 \times 10^{-19}\mathrm{J}}{1\ \mathrm{eV}} = 1.9 \times 10^{-19}\ \mathrm{J}$$

$$99.94\ \mathrm{eV} \cdot \frac{1.602 \times 10^{-19}\ \mathrm{J}}{1\ \mathrm{eV}} = 1.601 \times 10^{-17}\ \mathrm{J}$$

References

[1] Brown T L, LeMay Jr H E, Bursten B E, Burdge J R. Chemistry: the central science: ninth edition [M]. New Jersey: Pearson Education, Inc., 2003.

[2] Petrucci R H, Harwood W S, Herring F G. General chemistry: principles and modern applications: eighth edition [M]. New Jersey: Prentice - Hall, Inc., 2002.

[3] Silberberg M S. Chemistry: The molecular nature of matter and change: third edition [M]. New York: McGraw Hill Company, 2003.

[4] Gilbert T R, Kirss R V, Foster N, Davies G. Chemistry: second edition [M]. New York: W. W. Norton & Company Inc., 2009.

[5] Oxtoby D W, Freeman W A, Block T F. Chemistry: science of change: fourth edition [M]. California: Brooks/Cole - Thomson Learning, 2003.

[6] Olmsted III J, Williams G M. Chemistry: third edition [M]. New York: John Wiley & Sons, Inc., 2002.

[7] Taylor J R. An introduction to error analysis: the study of uncertainties in physical measurements [M]. Sausalito: University Science Books, 1999.

[8] Skoog D A, West D M, Holler F J, Crouch S R. Analytical chemistry: an introduction, seventh edition [M]. Belmont: Thomson Brooks/Cole, 1999.

[9] Harvey D. Modern analytical chemistry [M]. Boston: McGraw - Hill Companies,

Inc., 2000.

[10] http://www.chem1.com/acad/webtext/pre/matter.html.

[11] http://www.tutorvista.com/content/chemistry/chemistry - iii/chemistry - concepts/matter - classification.php.

[12] http://step.nn.k12.va.us/science/physci/ppt/classes_of_matter.ppt.

[13] http://www.chem.sc.edu/faculty/morgan/resources/sigfigs/index.html.

[14] http://antoine.frostburg.edu/cgi - bin/senese/tutorials/sigfig/index.cgi.

[15] http://physics.nist.gov/cuu/Units/index.html.

[16] http://www.bipm.org/utils/common/pdf/si_brochure_8_en.pdf.

[17] http://en.wikipedia.org/.

[18] http://chemistry.about.com/.

[19] http://library.thinkquest.org/3659/intro/measures.html.

[20] http://www.chem1.com/acad/webtext/pre/mm1.html.

[21] http://www.800mainstreet.com/2/0002 - 000 - TOC.html.

[22] http://www.alysion.org/dimensional/fun.htm.

[23] http://www4.ncsu.edu/unity/lockers/users/f/felder/public/kenny/papers/units.html.

[24] http://wshs.wtvl.k12.me.us/~science/rsmith/Unit%20PowerPoints/PP1.ppt.

[25] http://e - learning.njut.edu.cn/vod/3194786.pdf.

Chapter 2 Nomenclature of Inorganic Chemistry

2.1 Chemical Language

The subjects of naming chemical substances, or *chemical nomenclature*, and writing chemical "equations" are basic to communication in the society of chemists. The language of chemistry has evolved and improved with the understanding of chemical principles. For this reason, an understanding of chemical language in not only useful for communicating, but reflects an underlying understanding of the concepts of chemistry. The ability to name common chemical compounds is absolutely essential for success in a general chemistry course.

Chemical language is similar to other human languages, with element symbols forming the alphabet, chemical formulas the words, chemical equations the sentences and multistep chemical processes the paragraphs. Commercial production processes are chapters in the story of chemistry. Genetics, pollution and disease comprise entire volumes. Abbreviations and phonemes are (unfortunately) extensively used also, particularly in areas where long, complicated names are found, such as organic chemistry and biochemistry. Story setting corresponds to the reaction conditions, and plot development to reaction yields and pathways. We shall explore a number of chemical grammars and show how to solve simple problems related to structure and nomenclature.

Unfortunately, partly due to historical precedent and conceptual limitations, there is no ultimate chemical language which describes uniquely everything known about a material, including molecular structure and chemical properties, and it may be assumed that chemical concepts yet to be discovered will lead to new ways of describing that knowledge. For this reason, *several different systems of terminology are in use today*, each with advantages and disadvantages. The best we can do here is to introduce a few communication methods students are likely to encounter in introductory courses.

2.2 Nomenclature of Elements

2.2.1 Chemical Symbol

A **chemical symbol** is an abbreviation or shortened version of the name of a chemical element. Each element has its own unique symbol. A symbol both identifies a specific element and represents an atom of that element.

The use of a chemical symbol to represent a chemical substance goes back to ancient times. Alchemists had designed arcane symbols for both metals and common compounds. The present symbols express the system set out by the atomic theory of matter. John Dalton first used symbols to designate single atoms of elements. He probably used a circle for each because, like the ancient Greeks, he thought of atoms as tiny, round hard indivisible spheres. During the first half of the nineteenth century, an outstanding Swedish chemist, Jöns Jacob Berzelius, systematically assigned letters as symbols for the elements. This method soon became accepted by chemists everywhere. In 1921 the **International Union of Pure and Applied Chemists** (**IUPAC**) established the **Commission on the Nomenclature of Inorganic Chemistry** (**CNIC**). Rules for accepting element names were established in 1938 with revisions in 1957 and 1970. Today, the **IUPAC** is the organization that makes the final decision on the names and symbols of the element.

Chemical symbols are composed of one or two letters. There are about a dozen common elements that have a single capitalized letter for their symbol. The rest, that have permanent names have two letters. The first is capitalized and the second is lower case. The lower case letter is either the second letter in the name, or the letter of a strong consonant heard when the name of the element is spoken.

Most of the elements have symbols derived from their English name, but a few symbols stem from other languages. Ten of the elements have symbols from their Latin names and one element with a symbol from a German name.

IUPAC has recently prescribed that "aluminium" and "caesium" take the place of the US spellings "aluminum" and "cesium", while the US "sulfur" takes the place of the British "sulphur".

2.2.2 Names and Origins of Elements

The first 112 elements have internationally accepted names, which are derived from the compound or substance in which the element was discovered; an unusual or identifying property of the element; places, cities, and countries; famous scientists; Greek mythology and astronomical objects.

1. Substances Known by Alchemists

Carbon (**C=#6**): The name derives from the Latin *carbo* for *charcoal*.

Sulfur (**S=#16**): The origin of the English word is the Latin word *sulphurium* which comes from Sanskrit *sulveri* meaning to burn slowly.

Iron (**Fe=#26**): Iron was known of from ancient times and its name is of Anglo-Saxon origin. The symbol "Fe" is derived from the Latin word *ferrum* for *iron*.

Copper (**Cu=#29**): Copper was known in ancient Rome as *aes cyprium* meaning *ore from Cyprus*. The name later mutated to "**cuprum**" from which its symbol is derived.

Silver (**Ag=#47**): The word *silver* is of obscure Anglo-Saxon origin. The old Sanskrit word *argunas*, meaning *shining brightly*, mutated into the Latin word "**Argentum**" from which the symbol "**Ag**" is derived.

Tin (**Sn=#50**): The English name **Tin** is of unknown origin, perhaps *tina* (Germanic) for shiny little stick. The Latin name **Stannum** is connected to *stagnum* and *stag* (Indo-European) for dripping because Tin melts easily.

Platinum (**Pt=#78**): Platinum was known of and used by pre-Columbian Indians. Spanish mathematician Don Antonio de Ulloa named the metal *platina* meaning *silver-like* or *little silver* in 1748. Platinum looks like silver.

Gold(**Au=#79**) is the old Anglo-Saxon designation for this precious metal and has roots in Sanskrit (*Jval* which means *shining*). The chemical symbol **Au** derives from the Latin **Aurum**, for *Aurora* the Goddess of dawn.

Mercury(**Hg=#80**): The name for the liquid metal, **Mercury**, is from the easily flowing Roman god of messengers and the fast moving planet, both of the same name. **Hydrargyrum** from *hydro-argyros* (Greek) for *water-silver* since mercury is a shiny liquid.

Lead (**Pb=#82**): The English name **Lead** is of unknown origin, but perhaps related to *lodd* (Norse) and *Lot* (Germanic). **Plumbum**: Lead was called *plumbum nigrum* (black lead) by the Romans to distinguish it from *plumbum candidum* (light lead, now called Tin). *Plumbum* (Latin) is possibly related to *Molybdos* (Greek) also meaning lead.

2. Elements Named for Color

Chlorine (Cl= #17):Chlorine is a greenish-yellow (also toxic and aggressive) gas. *Chloros* is Greek for *greenish yellow*.

Chromium(Cr= #24): Chromium is responsible for the many different colors of its compounds – its name is derived from the Greek word *chroma* for *color*.

Rubidium(Ru= #44): Rubidium has deep-red emission lines in its spectrum. For that reason it was named after the Latin word *rubidis* for *deep-red*.

Rhodium (Rh= #45): Rhodium forms rose-coloured compounds. It is named after the Greek word *rhodon* for *rose*.

Indium (In= #49): Indium was identified spectroscopically due to its deep blue, or indigo-coloured emission line (*indigo* in its turn is named after the blue dye indigo, which was used by the ancient Greeks and Romans who named it *indikon* or *indicum* as the dye was imported from India).

Iodine (I= #53): Iodine is named after the Greek word *iodes* meaning *violet* because of the color of gaseous iodine.

Caesium (Cs = #55): Caesium was identified using spectroscopic methods in 1860. Caesius is Latin for sky blue, the color of the element's emission spectrum.

Iridium (Ir= #77): Iridium derives from the Latin word *iris* meaning *rainbow* because its salts show a variety of colors.

Thallium (Tl= #81): Thallium emits a sharp green line in its emission spectrum, and was named after the Greek word *thallus* meaning *sprouting green twig*.

3. Elements Named for Properties other than Color

Hydrogen (H= #1): *Hydros* (Greek) for water and-*gen* (Greek) meaning producing, was suggested by Lavoisier because when hydrogen burns, water is produced.

Nitrogen (N= #7) was derived from *Niter* (Greek) for saltpeter, combined with *-gen* (Greek), meaning producing.

Oxygen (O= #8): *Oksys* (Greek) for acid, & *-gen* (Greek) for producing.

Phosphorus (P= # 15): Its name derived from the Greek words *Phos* meaning light and *-phere* for bearing, since white phosphorus emits light in the dark.

Zinc (Zn= #30) may be derived from the German word *Zink* or *Zinke* which translates to *tine or sharp edge*. The mineral *calamine* (zinc carbonate) from which the metal can be obtained has many sharp edges.

Fluorine (F= #9): *Fluere* (Latin) means to flow.

Bromine (Br= #35): *Bromos* (Greek) meaning stink, or bad odor, describes the smell of the element Bromine. *-ine* is a suffix previously used for other halogens.

Antimony (Sb= #51): Antimony was thought not to be found alone in nature. Its name is derived from this assumption: *anti* and *monos* are Greek for *not* and (in this context) *alone*. While it is true that the element is predominantly found as a component in many minerals, it is also found in its elementary form. The Latin name **Stibium** from which the symbol **"Sb"** is comes from the mineral *stibnite* (antimony sulfide) in which it occurs. *Stibni* is Greek for *mark* because this mineral was used as a black pigment.

Osmium (Os= #76): Its oxide is volatile and has a sharp smell. For this reason the element was named after the Greek word *osme* meaning *smell*.

4. Elements Named after "Modern" Celestial Objects

Helium (He= #2)for *Helios*, the (Greek) name for the sun.

Selenium (Se= #34): *Selene* is the (Greek) name for the moon.

Palladium (Pd= #46): *Pallas* (Athene), the second asteroid. Pallas was the Greek goddess of wisdom.

Tellurium (Te= #52):Tellurium was named after the Roman goddess of the earth, *Telles*.

Cerium (Ce= # 58) was derived from that of *Ceres*, the first asteroid. Ceres was the Roman Goddess of corn and harvest.

Uranium (U= #92) was named after the planet *Uranus*. *Uranos* was the Greek god of the Heavens.

Neptunium (Np= # 93): It was the next element after Uranium on the periodic chart and the next planet after Uranus was *Neptune*. Neptune was the god of the seas.

Plutonium (Pu = # 94): The second element after Uranium on the periodic chart should be named for the second planet after Uranus, *Pluto*. Pluto was the god of the underworld.

5. Names Derived from Mythology or Superstition

Titanium (Ti= #22): Titanium has its obvious origin in the *Titans* who were, according to Greek mythology, the first sons of the earth.

Vanadium (V= #23): It was named after the Nordic goddess of love and beauty, Freya *Vanadis*.

Cobalt (Co= #27): *Kobold* (German) meant evil sprite.

Nickel (Ni= #28): *Nickel* (German) means devil or deceptive little spirits.

Arsenic (As= #33): *Arsenikos* (Greek) means brave, male.

Niobium (Nb= # 41): Niobium is named after *Niobe* the daughter of Tantalus in Greek mythology, because niobium is the lighter homologue of tantalum in the periodic table.

Promethium (Pm= # 61): *Prometheus* was the god who stole fire from heaven.

Tantalum (Ta= #73): Tantalum is named after *Tantalus*, the father of Niobe, was condemned to hell, standing to his neck in water.

Wolfram (W= #74): The element occurs in a mineral called *wolframite* (iron and manganese wolframate), from which it takes its official symbol and worldwide most common name, wolfram. The name "wolframite" comes from the German translation of *lupi spuma* (*Wolf Rahm*) which means *wolf's foam*. This name was given as during the extraction process it "eats" tin like a wolf eats sheep. **Tungsten** derives from the Swedish *tung sten* which means *heavy stone*. Tungsten also used to be the name of the mineral in which the element occurs (calcium wolframate), which forms very heavy stones.

Thorium (Th= #90): *Thor*, the Norse god of war.

6. Elements Named for People

Curium (**Cm**=＃ **96**): It was named after **Pierre** and **Marie Curie**, who discovered Radium and researched radioactivity.

Einsteinium (**Es**=＃ **99**): It was named after **Albert Einstein** (1879 - 1955), for his work on theoretical physics including the photoelectric effect.

Fermium(**Fm** =＃ **100**): It was named in honor of **Enrico Fermi** (1901 - 1954), who developed the first nuclear reactor, quantum theory, nuclear and particle physics, and statistical mechanics.

Mendelevium (**Md**=＃ **101**): Named in honor of **Dmitri Mendeleev**, who invented periodic table.

Nobelium (**No**=＃ **102**): Named in honor of **Alfred Nobel**, who invented dynamite and instituted the Nobel Prizes foundation.

Lawrencium (**Lr**= ＃ **103**): Named in honor of **Ernest O. Lawrence**, who was involved in the development of the cyclotron.

Rutherfordium (**Rf**=＃ **104**): Element ＃104 was made independently by an American group at Berkeley and a Russian group at Dubna. The Americans proposed the name after **Ernest Rutherford** . The Russians proposed the name **Kurtchatovium** (**Ku**) after **Igor Kurtchatov** (1903 - 1960), a Russian atomic physicist.

Seaborgium(**Sg**=＃ **106**): Named in honor of **Glenn T. Seaborg**, who discovered the chemistry of the transuranium elements, shared discovered and isolated 10 elements, developed and proposed the actinide series.

Bohrium (**Bh**=＃ **107**): Named in honor of **Niels Bohr**, who made fundamental understanding of atomic structure and quantum mechanics.

Meitnerium (**Mt**=＃ **109**): Named in honor of **Lise Meitner**, who shared discovery of nuclear fission.

Roentgenium (**Rg**=＃**111**): Named in honor of **Wilhelm Conrad Röntgen**, who produced and detected X-rays.

Copernicium (**Cn** = ＃ **112**): Named in honor of **Nicolaus Copernicus**. Copernicium was first created on February 9, 1996, at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany by Sigurd Hofmann, Victor Ninov et al. It was given its new name "copernicium" in February, 2010.

7. Elements Named for Locations of Ores

Magnesium (**Mg = # 12**): From *magnesia alba*, the white *magnesia* ($MgCO_3$) from *Magnesia* in ancient Greece.

Manganese (**Mn= #25**): From a dark brown half mineral from Germany called braunstein was known to color glass and pottery violet. It was also known as *magnesia nigri* meaning *black magnesia* (MnO_2) from *Magnesia* in ancient Greece.

Strontium (**Sr= #38**): The element was discovered in the earth *strontia*.

Cadmium (**Cd = # 48**), meaning *cadmium fornacum* or *furnace calamine*. *Calamine* ($ZnCO_3$) was an earth found in *Kadmeia* in Ancient Greece.

The following elements were discovered in earths separated from the dense, black mineral *gadolinite* (earlier called *ytterite*) found in the mine at **Ytterby**, a village near Stockholm, Sweden.

Yttrium (**Y= #39**) was named for its earth *yttria*.

Erbium (**Er= #68**) was named for its earth *erbia*.

Terbium (**Tb= #65**) was named for its earth *terbia*.

Ytterbium (**Yb= #70**) was named for its earth *ytterbia*.

Holmium (**Ho= #67**) and its earth *holmia* were named for *Holmium*, the ancient name for Stockholm.

Thulium (**Tm = # 69**) and its earth *thulia* were named after *Thule*, an ancient name for Scandinavia.

8. Elements Named for Geographical Places prior to the 20th Century

Scandium (**Sc= #21**): (Latin) for Scandinavia.

Gallium (**Ga= #31**): (Latin) for France.

Germanium (**Ge= #32**): after Germany.

Ruthenium (**Ru= #44**): From Latin *Ruthenia*, means Russia.

Europium (**Eu= #63**): after the Continent.

Lutetium (**Lu= #71**): Named after the Latin, *Lutetia*, the city of Paris.

Hafnium (**Hf= #72**): (Latin) for Copenhagen.

Rhenium (**Re= #75**): from Latin *Rhenus*, the river Rhine.

Polonium (**Po= #84**): for Poland.

Francium (**Fr= #87**): for France.

Americium (**Am=**＃**95**) was isolated in 1945 by **Seaborg**, **Ghiorso**, **Thompson** working in Chicago as part of the Manhattan Project.

Berkelium (**Bk=**＃**97**) was made in December 1949 at the University of California- *Berkeley* by Thompson, Ghiorso, and Seaborg.

Californium (**Cf=**＃**98**) was made in January 1950 at the University of *California* – Berkeley by Thompson, Street, Ghiorso, and Seaborg .

Dubnium (**Db=**＃**105**) was made in 1967 both at Berkeley and at the Russian Nuclear Institute at *Dubna*, north of Moscow.

Hassium (**Hs=**＃**108**) was named for the German State of *Hesse* (Latin for Germany: *Hassias*) where it was made.

Darmstadtium (**Ds=**＃**110**): On 9 November 1994 at 4:39 p.m., the first atom of the heaviest chemical element with atomic number 110 was detected at GSI in *Darmstadt*, Germany.

9. Elements Named for Minerals

Beryllium (**Be=**＃**4**): *Beryllos* (Greek) is the name of beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$.

Boron (**B=**＃**5**): *Bauraq* (Arabic) and *burah* (Persian) are names for *borax*, $Na_2B_4O_7 \cdot 10H_2O$.

Sodium (**Na=**＃**11**): *Suwwad* (Arabic) is a plant with high soda content (Na_2CO_3). *Sodanum* (Medieval Latin) was a headache remedy. *Natrium*: *Neter* (Hebrew) and *nitrum* (Latin) are ancient names for alkalies.

Aluminium (**Al=**＃**13**): *Alumen* (Latin) means *alum*. Alum was the name for $K_2Al_6(OH)_{12}(SO_4)_4$, which is used as an astringent from ancient times.

Silicon (**Si=**＃**14**): *Silex* (Latin) is flint, a hard stone.

Potassium (**K=**＃**19**): Because the metal was obtained from *potash* (K_2CO_3), Davy named the element **Potassium**. Potassium is called **Kalium** in German and Scandinavian languages which derive from *al-quali* (Arabic) meaning the ash.

Calcium (**Ca=**＃**20**): *Kylix* (Greek) = *calx* (Latin) means chalk.

Zirconium (**Zr=**＃**40**): *Zerk* (Arabic) means precious stone. Zirconium is in zircons, $ZrSiO_4$. *Zargum* (Arabic) means golden yellow colored.

Molybdenum (**Mo=**＃**42**): Before 1600, soft black minerals (graphite,

Sb_2S_3, PbS, MoS_2) that leave black marks were all called *molybdos*, *molybdän*, or *molybdenum*. Scheele called the metal that formed **Molybdenum** since *Molybdos* was Greek for lead.

Barium (Ba= #56): The mineral ($BaSO_4$) became known as *baryte* and the alkalie *baryta* after the (Greek) *barys* meaning heavy.

Samarium (Sm= #62): *samaria*.

Gadolinium (Gd= #64), mineral *gadolinite*.

10. Names Constructed from other Words

Lithium (Li= #3): *Lithos* (Greek) means stone.

Technetium (Tc= #43): The element was named after the Greek word *techous* which means *artificial*. Technetium was the first element artificially produced.

Lanthanum (La= #57): *Lanthano* (Greek) means to hide or to escape notice.

Praseodymium(Pr= #59): *Praseios*, (Greek) for leek-green since it has greenish salts, and *didymos* meaning twin and **Neodymium (Nd= #60)** *Neos* (Greek) means new.

Dysprosium (Dy= #66): *Dysprositos* (Greek) means difficult to attain.

Bismuth(Bi = # 83): *Wiese* (German) for field and *Muten* (German) means to apply for mineral rights or perhaps *Weisse Masse* (German) means white mass.

Astatine (At= #85): Astatine is an unstable, synthetic element. *A-statos* (Greek) means *not standing or not lasting*. *-ine* denotes Astatine is a member of the halogen family.

Radium (Ra= #88): *Radius* (Latin) means ray.

Actinium (Ac= #89): *Aktinos* (Greek) means ray.

Protactinium (Pa= #91): *Protos* (Greek) meaning *prior* was combined with the name of the daughter element, **Actinium.** The name describes its decay to actinium (*proto* is Greek for *first*).

Neon (Ne= #10): *Neos* (Greek) means new.

Argon (Ar= # 18): the lazy one, because Argon is chemically inert. *Aergon* (Greek) means no work or no action.

Krypton (Kr= #36): *Kryptos* (Greek) means hidden.

Xenon (Xe= #54): *Xenos* (Greek) means the stranger.

Radon (Rn= #86): *Radius* (Latin) means ray.

11. Systematic Nomenclature and Symbols for New Elements

In the past, some elements were given two names because two groups claimed to have discovered them. To avoid such confusion it was decided in 1947 that after the existence of a new element had been proved beyond reasonable doubt, discoverers had the right to suggest a name to IUPAC, but that only the Commission on Nomenclature of Inorganic Chemistry (CNIC) could make a recommendation to the IUPAC Council to make the final decision. Names for elements up to and including element 103 do not, therefore, carry any implication regarding priority of discovery.

Newly discovered elements may be referred to in the scientific literature but until they have received permanent names and symbols from IUPAC, temporary designators are required. Such elements may be referred to by their atomic numbers, as in "element 120" for example, but IUPAC has approved a systematic nomenclature and series of three-letter symbols.

The name is derived directly from the atomic number of the element using the following numerical roots:

0 = nil
1 = un
2 = bi
3 = tri
4 = quad
5 = pent
6 = hex
7 = sept
8 = oct
9 = enn

The roots are put together in the order of the digits which make up the atomic number and terminated by "ium" to spell out the name. The final "n" of "enn" is elided when it occurs before "nil", and the final "i" of "bi" and of "tri" when it occurs before "ium". The symbol for the element is composed of the initial letters of the numerical roots which make up the name. For example, **element #104** should be called **Unnilquadium**: (Latin) **un=1**, **nil=0**, **quad=4**, with the ending **-ium** denoting a metal. The symbol would be the three letter abbreviation **Unq**.

Unnilquadium (#104=Unq) is now called **Rutherfordium (Rf).**

Unnilpentium (#105=Unp) is now called **Dubnium (Db)**.

Unnilhexium (#106=Unh) is now called **Seaborgium (Sg)**.

Unnilseptium (#107=Uns) is now called **Bohrium (Bh)**.

Unniloctium (# **108=Uno**) is now called **Hassium** (**Hs**).

Unnilennium (# **109=Une**) is now called **Meitnerium** (**Mt**) .

Ununnilium (# **110=Uun**) is now called **Darmstadtium** (**Ds**).

Unununium (# **111=Uuu**) is now called **Roentgenium** (**Rg**).

Ununbium (# **112=Uub**) is now called **Copernicium** (**Cn**).

Ununtrium (# **113=Uut**) was formed by the alpha emission from element #115.

Ununquadium (# **114=Uuq**): Only one atom of element #114 was made through a nuclear reaction involving fusing a Calcium ion with a Plutonium atom.

Ununpentium (# **115=Uup**): Scientists at Lawrence Livermore National Laboratory, in collaboration with researchers from the Joint Institute for Nuclear Research (JINR) in Dubna, Russia announced on February 2, 2004, the discovery of element #115 and subsequent alpha decay to element #113.

Ununhexium (# **116=Uuh**): On December 6, 2000, scientists working at the Joint Institute for Nuclear Research in Dubna, Russia, along with scientists from the U.S. Department of Energy's Lawrence Livermore National Laboratory, announced the creation of ununhexium. They produced ununhexium by bombarding atoms of curium - 248 with ions of calcium - 48. This produced ununhexium - 292, an isotope with a half - life of about 0.6 milliseconds (0.0006 seconds), and four free neutrons.

Ununseptium (# **117=Uus**): A team of Russian and American scientists produced six atoms of the element by smashing together isotopes of calcium and a radioactive element called berkelium in April of 2010.

Ununoctium (# **118=Uuo**): On October 16, 2006, scientists working at the Joint Institute for Nuclear Research in Dubna, Russia, along with scientists from the U.S. Department of Energy's Lawrence Livermore National Laboratory, announced the creation of ununoctium. They produced ununoctium by bombarding atoms of californium - 249 with ions of calcium - 48. This produced ununoctium - 294, an isotope with a half-life of about 0.89 milliseconds (0.00089 seconds), and three free neutrons. The californium target was irradiated with a total of 1.6×10^{19} calcium ions over the course of 1080 hours, resulting in the production of three atoms of ununoctium.

2.2.3 Names for Groups of Elements, and Their Subdivisions

Collective names of groups of like elements are used by IUPAC to describe nomenclature for categorization of chemical elements. The following names are approved by IUPAC:

Alkali metals – The metals of group 1: Li, Na, K, Rb, Cs, Fr.

Alkaline earth metals – The metals of group 2: Be, Mg, Ca, Sr, Ba, Ra.

Pnicogens – The elements of group 15: N, P, As, Sb, Bi.

Chalcogens – The elements of group 16: O, S, Se, Te, Po.

Halogens – The elements of group 17: F, Cl, Br, I, At.

Noble gases – The elements of group 18: He, Ne, Ar, Kr, Xe, Rn.

Lanthanoids – Elements 57 – 71: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

Actinoids – Elements 89 – 103: Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

Rare earth elements – Sc, Y, and the lanthanoids.

Transition metals – Elements in groups 3 to 12.

The generic terms **pnictide**, **chalcogenide**, and **halogenide** (or **halide**) are used in naming compounds of the pnictogens, chalcogens, and halogens.

2.2.4 Notes

(1)The isotopes ^{2}**H** and ^{3}**H** are named **deuterium** and **tritium** and the symbols **D** and **T** respectively may be used.

(2)The isotopes of an element except hydrogen should all bear the same name and are designated by mass numbers. For example, the atom of atomic number 8 and mass number 18 is named oxygen – 18 and has the symbol ^{18}O.

(3)For the elements gold, iron and wolfram, the names shall always be used when forming names derived from those of the elements, e.g. aurate, ferrate, tungstate and not goldate, ironate, wolframate.

(4)For some compounds of **sulfur**, **nitrogen** and **antimony**, derivatives of the Greek name **eiov**, the French name **azote**, and the Latin name **stibium** respectively, are used.

(5) The name **mercury** should be used as the root name also in language where the element has another name (mercurate, not hydrarygrate).

(6) Any new metallic elements should be given names ending in **-ium**. **Molybdenum** and a few other elements have long been spelt without an "i" in most languages, and the Commission hesitates to insert it.

2.3 Nomenclature of Inorganic Compounds

2.3.1 Common Names

Early chemical characterizations could not be based on chemical composition, which usually wasn't known, but rather on properties, such as color, taste, therapeutics (real or imagined), or origin. Substances were classified by *value* such as base (low), noble (high), regalus (kingly), by *taste* (a dangerous process) as with acids (sour), alkalies (bitter) or salts (salty), by *appearance* as with metals (lustrous), earths (insoluble) or airs (gaseous) and by *preparation* as with spirits (distillates), calxes (combustates), flowers (sublimates), coagulates (precipitates) or amalgams (combinates). These nonsystematic naming methods were often confusing, as a given substance might have several names, and the same name could be used for several substances. For example, what is known today as potassium carbonate was named after to a variety of sources as *Salt of Wormwood*, *Salt of Tartar*, *spodium*, *fixed alkali salt*, *potash*, etc. The common names and systematic names of some other compounds are listed in Table 2.1. As the understanding of matter improved, more systematic names began to be developed.

Table 2.1 Common and Systematic Names of Some Compounds

Formula	Common Name	Systematic Name
H_2O	Water	Dihydrogen monoxide
NH_3	Ammonia	Trihydrogen nitride
CO_2	Dry ice	Solid carbon dioxide
NaCl	Table salt	Sodium chloride

Continued

Formula	Common Name	Systematic Name
N_2O	Laughing gas	Dinitrogen monoxide
$CaCO_3$	Marble, chalk, limestone	Calcium carbonate
CaO	Quicklime	Calcium oxide
$Ca(OH)_2$	Slaked lime	Calcium hydroxide
$NaHCO_3$	Baking soda	Sodium hydrogen carbonate
$Na_2CO_3 \cdot 10H_2O$	Washing soda	Sodium carbonate decahydrate
$MgSO_4 \cdot 7H_2O$	Epsom salt	Magnesium sulfate heptahydrate
$Mg(OH)_2$	Milk of magnesia	Magnesium hydroxide
$CaSO_4 \cdot 2H_2O$	Gypsum	Calcium sulfate dihydrate
H_2SO_4	Battery acid	Sulfuric acid
$C_{12}H_{22}O_{11}$	Sugar	Sucrose
$C_9H_8O_4$	Aspirin	Acetylsalicylic acid

2.3.2 IUPAC Nomenclature

The IUPAC nomenclature of inorganic chemistry is a systematic method of naming inorganic chemical compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC). Ideally, every inorganic compound should have a name from which an unambiguous formula can be determined.

1. Naming Binary Molecular Compounds

Binary molecular compounds are formed between two nonmetals.

(1)The first element in the compound is named directly after its element name. If there is more than one atom of the element present in the molecule, then a numerical prefix must be added to the name. Common prefixes are given in Table 2.2.

(2)The second element in the compound is named after its element but the ending of the name is removed and an *-ide* is added (based on how it sounds), a prefix should always be used to show how many atoms of that element are present in the molecule (even if there is only one). Some common roots are listed in Table 2.3.

Table 2.2 Number Prefixes for Chemical Names

Number	Prefix	Number	Prefix
1	mono	9	ennea
2	di	10	deca
3	tri	11	undeca
4	tetra	12	dodeca
5	penta	20	eicosa
6	hexa	1/2	hemi
7	hepta	3/2	sesqui
8	octa		

Table 2.3 Common Roots for Naming Compounds

Element	Root	Element	Root
arsenic	arsen	iodine	iod
bromine	brom	manganese	mangan
carbon	carb	nitrogen	nitr
chlorine	chlor	oxygen	ox
chromium	chrom	phosphorus	phosph
fluorine	fluor	selenium	selen
hydrogen	hydr	sulfur	sulf or sulfur

Examples:

Formula	Name	Formula	Name
CO	carbon monoxide	CO_2	carbon dioxide
NO	nitrogen monoxide	NO_2	nitrogen dioxide
N_2O	dinitrogen monoxide	N_2O_3	dinitrogen trioxide
N_2O_4	dinitrogen tetroxide	N_2O_5	dinitrogen pentoxide
SO_2	sulfur dioxide	SO_3	sulfur trioxide
AsF_5	arsenic pentafluoride	N_2Cl_4	dinitrogen tetrachloride
SiO_2	silicon dioxide	CCl_4	carbon tetrachloride
PCl_5	phosphorus pentachloride	BrF_5	bromine pentafluoride

Note that when prefixes ending in *o*- or *a*- (like *mono*- and *tetra*-) precede a name that begins with a vowel such as oxide, the *o* or *a* at the end of the prefix is deleted to make the combination of prefix and name easier to pronounce.

This pattern holds for all binary molecular compounds. The order in which the elements are named and given in formulas corresponds to the relative positions of the elements in the periodic table: the element with the lower group number (that is, to the left of the other) appears first in the name and formula. When both elements are in the same column — for example, sulfur and oxygen — then the name of the element with the higher atomic number (that is, lower in the column) appears first.

Hydrogen requires special consideration because it may appear first or second in the formula and name of a compound. With elements from Groups 1 and 17, hydrogen forms diatomic molecules names according to the guidelines. With elements from Groups 12 and 16, hydrogen forms compounds containing two atoms. Except for oxygen, there is only one commonly occurring binary compounds for each element, so the prefix *di*- is omitted. Oxygen forms two binary compounds with hydrogen. One is water, H_2O, the other is hydrogen peroxide, H_2O_2. The binary compounds of hydrogen with elements from Group 13 through 15 have unsystematic names, some of them are listed below. Carbon, boron and silicon form many different binary compounds with hydrogen; only the simplest is listed.

Unsystematic names:

NH_3: ammonia (nitrogen hydride)
AsH_3: arsine (arsenic hydride)
SiH_4: silane
$COCl_2$: phosgene (carbonyl chloride)
PH_3: phosphine (phosphorus hydride)
B_2H_6: diborane
CH_4: methane

2. Naming Binary Ionic Compounds

A binary ionic compound consists of a positively charged cation formed by a metallic element and a negatively charged anion formed by a nonmetal. The names of binary ionic compounds begin with the name of the cation, which is simply the name of the parent element. This is followed by the name of the anion, which is the name of the element, except that the last syllable of that element's name is replaced with *-ide*.

Prefixes are not used in the names of salts of representative elements because the metal ions in the main groups (group 1, 2, and aluminum in group 13) typically make only one cation. For example, magnesium (group 2) forms only a 2+ cation. Correspondingly the nonmetallic halogens (group 17) as anions have a charge of 1−; nonmetallic anions from group 16 are 2−, and those from group 15 are 3−. Ionic compounds are electrically neutral, so the negative and positive charges of the ions in an ionic compound must balance.

Examples:

Formula	Name	Formula	Name
$NaCl$	sodium chloride	KI	potassium iodide
NaF	Sodium fluoride	MgF_2	magnesium fluoride
$BaCl_2$	barium chloride	Na_2S	sodium sulfide
K_2O	potassium oxide	Al_2O_3	aluminum oxide

Some metallic elements, including many of the transition metals in the middle of the periodic table, form cations with several different charges. For example, most of the copper found in nature is present as Cu^{2+}; however, some copper compounds contain Cu^{+}. Thus the name copper chloride could apply to $CuCl_2$ or $CuCl$. Systematic names are needed to distinguish between the two compounds. One system uses a Roman numeral that defines the charge on the cation after the word copper in the name of the compound. Thus copper(Ⅱ) chloride represents the chloride of Cu^{2+}, which is $CuCl_2$. The formula of copper(Ⅰ) chloride is $CuCl$. Chemists have for many years also used different names to identify cations of the same element with different charges. Cu^{+} compounds are called *cuprous*, and Cu^{2+} compounds are called *cupric*. Similarly, the typical ions of iron — Fe^{2+} and Fe^{3+} — are called ferrous and ferric, respectively. Table 2.4 lists the common cations with more than one charge. Note that, the name of the ion with the lower charge ends in *-ous* and the name of the one with the higher charge ends in *-ic*. You must determine the charged state based on the other element in the compound.

Examples:

Formula	IUPAC Name	Common Name
FeO	iron(Ⅱ) oxide	ferrous oxide
Fe_2O_3	iron(Ⅲ) oxide	ferric oxide
Cu_2S	copper(Ⅰ) sulfide	cuprous sulfide
CuS	copper(Ⅱ) sulfide	cupric sulfide
SnF_2	tin(Ⅱ) fluoride	stannous fluoride
SnF_4	tin(Ⅳ) fluoride	stannic fluoride
Hg_2Br_2	mercury(Ⅰ) bromide	mercurous bromide
$HgBr_2$	mercury(Ⅱ) bromide	mercuric bromide

Table 2.4 Some Common Cations with More Than One Charge

IUPAC Name	Common Name	Symbol	IUPAC Name	Common Name	Symbol
bismuth(Ⅴ)	bismuthic	Bi^{5+}	mercury(Ⅱ)	mercuric	Hg^{2+}
chromium(Ⅱ)	chromous	Cr^{2+}	iron(Ⅱ)	ferrous	Fe^{2+}
chromium(Ⅲ)	chromic	Cr^{3+}	iron(Ⅲ)	ferric	Fe^{3+}
cobalt(Ⅱ)	cobaltous	Co^{2+}	nickel(Ⅱ)	nickelous	Ni^{2+}
cobalt(Ⅲ)	cobaltic	Co^{3+}	nickel(Ⅲ)	nickelic	Ni^{3+}
copper(Ⅰ)	cuprous	Cu^{+}	platinum(Ⅱ)	platinous	Pt^{2+}
copper(Ⅱ)	cupric	Cu^{2+}	platinum(Ⅳ)	platinic	Pt^{4+}
gold(Ⅰ)	aurous	Au^{+}	thallium(Ⅰ)	thallous	Tl^{+}
gold(Ⅲ)	auric	Au^{3+}	thallium(Ⅲ)	thallic	Tl^{3+}
lead(Ⅱ)	plumbous	Pb^{2+}	tin(Ⅱ)	stannous	Sn^{2+}
lead(Ⅳ)	plumbic	Pb^{4+}	tin(Ⅳ)	stannic	Sn^{4+}
manganese(Ⅱ)	manganous	Mn^{2+}	titanium(Ⅲ)	titanous	Ti^{3+}
manganese(Ⅲ)	manganic	Mn^{3+}	titanium(Ⅳ)	titanic	Ti^{4+}
mercury(Ⅰ)	mercurous	Hg_2^{2+}			

3. Naming Ionic Compounds Involving Polyatomic Ions

Table 2.5 lists the names and chemical formulas of some commonly encountered ions. Most of them are **polyatomic** ions; that is, they consist of more than one kind of atom joined by covalent bonds. The **ammonium** ion (NH_4^+) is the only common cation among the polyatomic ions; all the others are anions.

Polyatomic ions containing oxygen and one or more other elements are called **oxoanions**. Each oxoanion has a name based on the name of the element that appears first in the formula, but the ending is changed to either *-ite* or *-ate*, depending on the number of oxygen atoms in the formula. Thus, SO_4^{2-} is **sulfate** whereas SO_3^{2-} is **sulfite**. The sulfate ion has one more oxygen atom than the sulfite ion. The general rule, that ions with names ending in *-ate* have one more oxygen than those whose names end in *-ite*, applies to naming the oxoanions of nitrogen, **nitrate** (NO_3^-) and **nitrite** (NO_2^-), and to naming other sets of oxoanions.

Table 2.5 Names and Charges of Some Common Polyatomic Ions

Name	Symbol	Name	Symbol	Name	Symbol
acetate	CH_3COO^-	amide	NH_2^-	ammonium	NH_4^+
arsenate	AsO_4^{3-}	arsenite	AsO_3^{3-}	azide	N_3^-
borate	$B_4O_7^{2-}$	perbromate	BrO_4^-	bromate	BrO_3^-
bromite	BrO_2^-	hypobromite	BrO^-	bicarbonate	HCO_3^-
carbonate	CO_3^{2-}	perchlorate	ClO_4^-	chlorate	ClO_3^-
chlorite	ClO_2^-	hypochlorite	ClO^-	dichromate	$Cr_2O_7^{2-}$
chromate	CrO_4^{2-}	cyanate	OCN^-	cyanide	CN^-
ferricyanide	$Fe(CN)_6^{3-}$	ferrocyanide	$Fe(CN)_6^{4-}$	hydroxide	OH^-
permanganate	MnO_4^-	manganate	MnO_4^{2-}	nitrate	NO_3^-
hydronium	H_3O^+	dithionite	$S_2O_4^{2-}$	thiosulfate	$S_2O_3^{2-}$
nitrite	NO_2^-	oxalate	$C_2O_4^{2-}$	peroxide	O_2^{2-}
phosphate	PO_4^{3-}	phosphite	PO_3^{3-}	sulfate	SO_4^{2-}
sulfite	SO_3^{2-}	thiocyanate	SCN^-	dithionate	$S_2O_6^{2-}$

If an element forms more than two kinds of oxoanions, as chlorine and the other group 17 elements do, prefixes are used to distinguish them. The oxoanion with the largest number of oxygen atoms gets the prefix *per* - , and that with the smallest number of oxygen atoms may have the prefix *hypo* - in its name. Note that these rules do not enable you to predict the chemical formula from the name or the charge on the anion. You need to memorize the formulas, charges, and names of the common oxoanions such as those of chlorine, sulfur, and phosphorus.

Anions derived by adding H^+ to an oxoanion are named by adding as a prefix the word *hydrogen* or *dihydrogen*, as appropriate:

HCO_3^- : hydrogen carbonate	HSO_4^- : hydrogen sulfate
HPO_4^{2-} : hydrogen phosphate	$H_2PO_4^-$: dihydrogen phosphate

4. Naming Acids

An ***acid*** can be defined as a substance that yields hydrogen ions (H^+) — sometimes referred to as protons—when dissolved in water.

(1)Acids based on anions whose names end in *-ide*.

Acids giving rise to the *-ide* anions defined as binary and pseudobinary compounds of hydrogen, e. g. hydrogen chloride, hydrogen sulfide, hydrogen cyanide. Hydrogen chloride is a binary compound. When dissolved in water, this compound produces an acidic solution, which we call *hydrochloric acid*. In naming this and other acids based on anions whose names end in *-ide*, the following guidelines apply:

①Affix the prefix *hydro* - to the name of the element other than hydrogen in the molecule.

②Replace the last syllable in the name with the suffix *-ic* and add *acid*.

Examples of acids based on anions whose names end in *-ide* are as follows:

Name	Symbol
Hydrofluoric Acid	HF
Hydrochloric Acid	HCl
Hydrobromic Acid	HBr

Continued

Name	Symbol
Hydroiodic Acid	HI
Hydrocyanic Acid	HCN
Hydrosulfuric Acid	H_2S

For the compound HN_3, the name *hydrogen azide* is recommended in preference to *hydrazoic acid*. This nomenclature may also be used for less common acids, e.g. *hexacyanoferrate* ions correspond to *hexacyanoferric acids*. In such cases, however, systematic names of the type *hydrogen hexacyanoferrate* are preferable.

(2) Acids based on oxoanions whose names end in *-ate* or *ite*.

Most of the common acids are *oxoacids*, i.e. they contain only oxygen atoms bound to the characteristic atom. It is a long-established custom not to indicate these oxygen atoms. It is mainly for these acids that long-established names will have to be retained. If the name of the oxoanion ends in *-ate*, the name of the corresponding acid ends in *-ic*; when the name of the oxoanion ends in *-ite*, the name of the corresponding acid ends in *-ous*. Thus SO_4^{2-} is the formula of sulfate, and H_2SO_4 is the formula of *sulfuric acid*. Similarly, NO_2^- is the formula of nitrite, and HNO_2 is the formula of *nitrous acid*. Table 2.6 lists the common acids that contain oxoanions.

Table 2.6 Common acids that contain oxoanions

Name	Symbol	Name	Symbol
Acetic Acid	$HC_2H_3O_2$	Arsenic Acid	H_3AsO_4
Arsenous Acid	H_3AsO_3	Boric Acid	H_3BO_3
Carbonic Acid	H_2CO_3	Perchloric Acid	$HClO_4$
Chloric Acid	$HClO_3$	Chlorous Acid	$HClO_2$
Hypochlorous Acid	$HClO$	Chromic Acid	H_2CrO_4
Dichromic Acid	$H_2Cr_2O_7$	Cyanic Acid	$HOCN$
Nitric Acid	HNO_3	Nitrous Acid	HNO_2
Oxalic Acid	$H_2C_2O_4$	Phosphoric Acid	H_3PO_4
Phosphorous Acid	H_3PO_3	Phthalic Acid	$H_2C_8H_4O_4$
Sulfuric Acid	H_2SO_4	Sulfurous Acid	H_2SO_3

Further distinction between different acids with the same characteristic element is in some cases affected by means of prefixes. This notation should not be extended beyond the cases listed below.

①The prefix *hypo*- is used to denote a lower oxidation state, and may be retained in the following cases:

$HClO$	hypochlorous acid
$H_2N_2O_2$	hyponitrous acid
$H_4P_2O_6$	hypophosphoric acid

②The prefix *per*- has been used to designate a higher oxidation state and is retained only for $HClO_4$, perchloric acid, and corresponding acids of the other element in Group 17. This use of the prefix *per*- should not be extended to elements of other Groups.

③The prefixes *ortho*- and *meta*- have been used to distinguish acids differing in the "content of water". The following names are approved:

H_3BO_3	Orthoboric acid
H_4SiO_4	Orthosilicic acid
H_3PO_4	Orthophosphoric acid
H_5IO_6	Orthoperiodic acid
$(HBO_2)_n$	Metaboric acid
$(H_2SiO_3)_n$	Metasilicic acid
$(HPO_3)_n$	Metaphosphoric acid

The prefix *pyro*- has been used to designate an acid formed from two molecules of an *ortho*-acid minus one molecule of water. Such acids can now generally be regarded as the simplest cases of *isopolyacids*. The trivial name *pyrophosphoric acid* may be retained for $H_4P_2O_7$, although *diphosphoric acid* is preferable.

The prefix *peroxo*-, when used in conjunction with the trivial names of acids, indicates substitution of —O— by —O—O—.

Acids derived from oxoacids by replacement of oxygen by sulfur are called *thioacids*.

Acids containing ligands other than oxygen and sulfur are generally designated according to the rules in coordination compounds.

5. Naming Bases

A ***base*** can be defined as a substance that yields hydroxide ions (OH^-) when dissolved in water. Bases are named like other ionic compounds: the positively charged cation is named first, followed by the polyatomic ion.

Examples:

$NaOH$	sodium hydroxide	KOH	potassium hydroxide
$Ba(OH)_2$	barium hydroxide	$Mg(OH)_2$	magnesium hydroxide

6. Naming Hydrates

Many ionic compounds that have a specific number of water molecules attached to each formula unit are called **hydrates**. In the solid, these water molecules (also called "waters of hydration") are part of the structure of the compound. The ionic compound (without the waters of hydration) is named first using the rules for naming ionic compounds. Greek prefixes are attached to the word "hydrate" to indicate the number of water molecules per formula unit for the compound. When the chemical formula for a hydrated ionic compound is written, the formula for the ionic compound is separated from the waters of hydration by a centered dot.

Examples:

$CuSO_4 \cdot 5H_2O$	copper(Ⅱ) sulfate pentahydrate
$CaSO_4 \cdot 2H_2O$	calcium sulfate dihydrate
$CaSO_4 \cdot 1/2H_2O$	calcium sulfate hemihydrate
$FeCl_3 \cdot 6H_2O$	iron(Ⅲ) chloride hexahydrate
$LiCl \cdot H_2O$	lithium chloride monohydrate

7. Naming Coordination Complexes

Coordination complexes are a special class of compound consisting of central metal ions surrounded with groups of covalently bonded atoms, called *ligands*. Metal ions are classified by the number of bonds to ligands they form, called the *coordination number*. Ligands are classified according to the number of bonds they form with the central ion: *monodentate*, *bidentate*, etc. for one, two, etc. bonds. Multiply-bound ligands are called *polyden-*

tates, or *chelates*. Complexes are classified by their geometries: *linear*, *square planar*, *tetrahedral*, *octahedral*, *trigonal bipyramidal*, etc. Isomers are distinguished by *cis-* and *trans-* prefixes, signifying ligand bonding at adjacent and opposite coordination metal sites, respectively.

The name of the metal is preceded by the names of the ligands in alphabetical order using Greek prefixes (*di*, *tri*, *tetra*, *penta*, etc.) to indicate multiple monodentate ligands of the same type, and Sanskrit prefixes (*bis*, *tris*, *tetrakis*, *pentakis*, etc.) to indicate multiple polyentate ligands. Cationic (positive charged) ligands have *ium* suffixes, anionic (negative charged) ligands have *o* suffixes, and neutral ligands unchanged with some notable exceptions for such as *aqua* for water, *ammine* for ammonia, *carbonyl* for carbon monoxide and *nitrosyl* for nitrogen monoxide.

Complexes may have positive, negative or neutral net charge, depending on the sum of the charges of the metal ions and ligands (which may be positive, negative or neutral themselves). Negative complex ions are given the suffix *ate*. Coordination *compounds* containing ionic parts consist of complex ions or inorganic ions; they are named like binary inorganic compounds, with the cationic parts preceding the anionic parts.

Complex naming rules are straightforward and may be organized into the following naming algorithm:

Procedure:

(1) Identify the complex ions given in square brackets in the formula. Name cations before anions, separated with a space. Append the suffix *ate* to complex anions.

(2) For each complex, name the ligands before the metal ions.

①Identify the ligands as inorganic and organic molecules. Certain parenthesized abbreviations are used to represent long names, such as *en* for bidentate ethylenediamine ($H_2NCH_2CH_2NH_2$), *edta* for tetradentate ethylenendiaminetetraacetato $\{(CH_2)_2[N(CH_2CO_2)_2]^{4-}\}$, and *ox* for bidentate oxalato $[(COO)_2^{2-}]$.

②Give cationic (positive charged) ligands *ium* suffixes, anionic (negative charged) ligands *o* suffixes, and leave neutral ligands unchanged, except for certain common substances such as *aqua* for water, *ammine* for ammonia, *carbonyl* for carbon monoxide and *nitrosyl* for nitrogen monoxide.

③List the ligands in alphabetical order using Greek prefixes (*di*, *tri*, *tetra*, *penta*, etc.) to indicate multiple monodentate ligands of the same type, and Sanskrit prefixes (*bis*, *tris*, *tetrakis*, *pentakis*, etc.) to indicate multiple polyentate ligands.

(3) For each complex, append the name of the metal ion to the list of ligands to which it is attached.

①Use Latin names for the metal ions of anionic complexes.

②Determine the charge on the metal ion by subtracting the sum of the ionic ligand charges from the total charge on the complex.

③Append the charge on each metal ion to its name using parenthesized Roman numerals.

Example: Name the complex compound $[Co(en)_2Br_2]Cl$.

(1) There is one bracketed complex ion. It is named before the inorganic chloride ion.

(2) The ligands in the complex cation are "*en*", which stands for the complicated neutral organic *ethylenediamine*, and inorganic negative Br^-, named *bromo*. Using a Sanskrit prefix and retaining the parentheses for the abbreviated ligand, the ligand portion is named *bis(ethylenediamine)dibromo*.

(3) The complex has charge +1, balancing the charge on the chloride ion. Since "*en*" has zero charge and each bromo has −1 charge, the charge on the cobalt metal ion $= +1 - (-2) = +3$.

The total name is *bis(ethylenediamine)dibromocobalt* (Ⅲ) *chloride*.

References

[1] Olmsted III J, Williams G M. Chemistry: third edition [M]. New York: John Wiley & Sons, Inc., 2002.

[2] Brown T L, LeMay Jr H E, Bursten B E, Burdge J R. Chemistry: the central science: ninth edition [M]. New Jersey: Pearson Education, Inc., 2003.

[3] Silberberg M S. Chemistry: The molecular nature of matter and change: third edition [M]. New York: McGraw Hill Company, 2003.

[4] Gilbert T R, Kirss R V, Foster N, Davies G. Chemistry: second edition [M]. New York: W. W. Norton & Company Inc., 2009.

[5] Petrucci R H, Harwood W S, Herring F G. General chemistry: principles and modern applications: eighth edition [M]. New Jersey: Prentice - Hall, Inc., 2002.

[6] Oxtoby D W, Freeman W A, Block T F. Chemistry: science of change: fourth edition [M]. California: Brooks/Cole - Thomson Learning, 2003.

[7] Ringnes V. Origin of the names of chemical elements [J]. Journal of Chemical Education, 1989, 66: 9.

[8] http://www.unm.edu/ ~ dmclaugh/PrinciplesPDF/10_Nomenclature.pdf.

[9] http://science.jrank.org/pages/6663/Symbol - Chemical.html.

[10] http://www.wikidoc.org/index.php/Chemical_element.

[11] http://http://www.tutorvista.com/bow/latin - names - and - symbol - of - elements.

[12] http://www.bbc.co.uk/dna/h2g2/A2654769.

[13] http://www.docstoc.com/docs/6124768/Chemical_element.

[14] http://www - d0.fnal.gov/hardware/cal/lvps_info/.../elements.pdf.

[15] http://web.me.com/dtrapp/Elements/elements.html.

[16] http://www.careerchem.com/NAMED/Elements - Names.pdf.

[17] http://www.etymonline.com/.

[18] http://en.wikipedia.org/wiki/.

[19] http://en.wikipedia.org/wiki/Collective_names_of_groups_of_like_elements.

[20] http://old.iupac.org/reports/provisional/abstract04/RB.../Chap3 - 3.04.pdf.

[21] http://www.iupac.org/publications/pac/2002/pdf/7405x0787.pdf.

[22] http://www.sciencedaily.com/releases/.../100224102231.htm.

[23] http://education.jlab.org/itselemental/ele116.html.

[24] https://publicaffairs.llnl.gov/news/.../NR - 06 - 10 - 03.html.

[25] http://www.sciencedaily.com/releases/2004/02/040203234610.htm.

[26] http://www.physorg.com/news80226997.html.

[27] http://en.wikipedia.org/wiki/IUPAC_nomenclature_of_inorganic_chemistry.

[28] http://www.miracosta.edu/home/dlr/naming.htm.

[29] http://www.chem.purdue.edu/gchelp/nomenclature/hydrates.htm.

[30] http://www.chemistry.wustl.edu/~edudev/LabTutorials/naming_coord_comp.html.

Chapter 3 Inorganic Chemistry

3.1 The Atomic Nature of Matter

3.1.1 Atomic Theory

Two extremely important laws about chemical reactions were well established by the end of the 18th century without referring to the notion of an atomic theory: the **law of mass conservation** and the **law of definite (or constant) composition.** The **law of mass conservation**, formulated by Antoine Lavoisier in 1789 on the basis of his combustion experiments, states that the total mass of substances in a chemical reaction remains constant (that is, the reactants have the same mass as the products). The **law of definite proportions** states that if a compound is broken down into its constituent elements, then the masses of the constituents will always have the same proportions, regardless of the quantity or source of the original substance.

John Dalton studied and expanded upon this previous work and developed the **law of multiple proportions**: if two elements can together form more than one compound, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small integers.

The modern view of atomic theory can be summarized in four general statements:

(1)All matter is composed of tiny particles called atoms.

(2)All atoms of a given element have identical chemical properties that are characteristic of that element.

(3)Atoms form chemical compounds by combining in whole-number ratios.

(4)Atoms can change how they are combined, but they are neither created nor destroyed in chemical reactions.

3.1.2 Structure of the Atom

An atom is an electrically neutral, spherical entity composed of a positively charged central **nucleus** surrounded by a cloud of negatively charged **electrons**. The atomic nucleus consists of positively charged **protons** and electrically neutral **neutrons**, except in the case of hydrogen-1, which is the only stable nuclide with no neutrons. The electrons of an atom are bound to the nucleus by the electromagnetic force. The magnitude of charge possessed by a proton is equal to that of an electron (e^-), but the signs of the charges are opposite. An atom is electrically neutral because the number of protons in the nucleus equals the number of electrons surrounding the nucleus. The nucleus makes up almost all of an atom's mass or weight.

An atom is classified according to the number of protons and neutrons in its nucleus: the number of protons determines the chemical element, and the number of neutrons determines the isotope of the element.

3.1.3 Atomic Number, Mass Number and Atomic Symbol

The **atomic number** (also known as the proton number) is the number of protons found in the nucleus of an atom and therefore identical to the charge number of the nucleus. It is conventionally represented by the symbol Z. All atoms of a particular element have the same atomic number, and each element has a different atomic number from that of any other element. In an atom of neutral charge, the atomic number is also equal to the number of electrons.

The total number of protons and neutrons in the nucleus of an atom is its **mass number** (A). The number of neutrons, N, is known as the neutron number of the atom; thus, $A = Z + N$. Since protons and neutrons have approximately the same mass (and the mass of the electrons is negligible for many purposes), the atomic mass of an atom is roughly equal to A. The atomic number (Z) is written as a left *subscript* and the mass number (A) as a left *superscript* to the symbol, so element X would be ${}^{A}_{Z}X$.

3.1.4 Isotopes and Atomic Masses of the Elements

Isotopes are different types of atoms of the same chemical element, each having a different number of neutrons. All atoms of an element are identical in *atomic number* but not in *mass number*. Isotopes of an element are atoms that have different numbers of neutrons and therefore different mass numbers. Carbon has three naturally occurring isotopes ^{12}C, ^{13}C and ^{14}C.

An isotope is specified by the name of the particular element followed by a hyphen and the mass number (e.g. helium-3, carbon-12, carbon-13 and iodine-131). When a chemical symbol is used, e.g. "C" for carbon, standard notation is to indicate the number of nucleons with a superscript at the upper left of the chemical symbol and to indicate the atomic number with a subscript at the lower left (e.g. $^{3}_{2}He$, $^{4}_{2}He$, $^{12}_{6}C$, $^{14}_{6}C$, $^{235}_{92}U$ and $^{239}_{92}U$).

The terms atomic mass and atomic weight are often used interchangeably, although, strictly speaking, they do not mean the same thing. The **atomic mass** (m_a) is the mass of specific isotope of a given atom, it may be considered to be the total mass of protons, neutrons and electrons in a single atom (when the atom is motionless). **Relative atomic mass** is a synonym for **atomic weight** and closely related to *average atomic mass* (but not a synonym for atomic mass), the weighted mean of the atomic masses of all the atoms of a chemical element found in a particular sample, weighted by isotopic *abundance*. **Standard atomic weight** refers to the mean relative atomic mass of an element in the local environment of the Earth's crust and atmosphere as determined by the IUPAC Commission on Atomic Weights and Isotopic Abundances. The **unified atomic mass unit** or **atomic mass unit** (u) is a unit of mass used to express atomic and molecular masses. The precise definition is that the atomic mass unit (u) is one twelfth of the mass of an isolated atom of carbon-12 (^{12}C) at rest and in its ground state. In other words, "A single atom of carbon-12 has a mass of 12 u exactly, by definition."

The isotopic makeup of an element is determined by mass spectrometry, a method for measuring the relative masses and abundances of atomic-scale particles very precisely.

3.1.5 Ions

An **ion** is an atom or molecule in which the total number of electrons is not equal to the total number of protons, giving it a net positive or negative electrical charge. An **anion** is an ion with more electrons than protons, giving it a net negative charge. Conversely, a **cation** is an ion with more protons than electrons, giving it a positive charge.

An ion consisting of a single atom is a **monatomic** ion. If it consists of two or more atoms, it is a **polyatomic** ion. Polyatomic ions containing oxygen, such as carbonate and sulfate, are called **oxyanions**. If an ion contains unpaired electrons, it is called a **radical ion**.

3.2 Electronic Structure of Atoms

3.2.1 The Nature of Light

Much of our present understanding of the electronic structure of atoms has come from analysis of the light emitted or absorbed by substances. **Light** is one form of *electromagnetic* (EM) *radiation* (also known as *radiant energy*) of a wavelength that is visible to the human eye (in a range from about 400 − 700 nm). In physics, the term light sometimes refers to electromagnetic radiation of any wavelength, whether visible or not. The wavelengths and the frequencies of electromagnetic radiation cover an immense range. Except for visible light, other forms of electromagnetic radiation include the gamma ray, X-ray, ultraviolet and infrared, microwave, and radio frequency. The speed of light and other forms of electromagnetic radiation in a vacuum is fixed at 299,792,458 $\mathrm{m \cdot s^{-1}}$ ($3.00 \times 10^8\ \mathrm{m \cdot s^{-1}}$ to three significant figures) by the current definition of the meter.

The wave nature of light was first illustrated through experiments on **diffraction** and **interference**. The wave properties of electromagnetic radiation are described by two interdependent variables: **Frequency** (ν, Greek *nu*) is the number of cycles the wave undergoes per second and is expressed in units of $\frac{1}{\text{second}}$ [$\mathrm{s^{-1}}$; also called hertz (Hz)]. **Wavelength** (λ, Greek *lambda*) is the distance between any point on a wave and the corresponding point on the next wave; that is, the distance the wave travels during one cycle. Wavelength is expressed in meters and often, for very short wavelengths, in

The constant h is called **Planck's constant** and has a value of 6.63×10^{-34} J • s. In the quantum theory, energy is quantized, meaning that it can have only certain allowed values. Einstein used the quantum theory to explain the **photoelectric effect**, the emission of electrons from metal surfaces by light. He pro-
its **amplitude**. The **amplitude** of a light wave is related to its **intensity**.

Max Planck proposed that the minimum amount of radiant energy that an object can gain or lose is related to the frequency of the radiation: $E = h\nu$. This smallest quantity is called **quantum** (meaning "fixed amount") of energy. The constant h is called **Planck's constant** and has a value of 6.63×10^{-34} J • s. In the quantum theory, energy is quantized, meaning that it can have only certain allowed values. Einstein used the quantum theory to explain the **photoelectric effect**, the emission of electrons from metal surfaces by light. He proposed that light behaves as if it consisted of quantized energy packets called **photons**. Each photon carries energy $E = h\nu$.

Dispersion of radiation into its component wavelengths produces a **spectrum** (plural: spectra). Although frequently associated with light, the term can be applied to any wave phenomena. A **continuous spectrum** is one in which every frequency is present within some range. A **discrete spectrum** or **line spectrum** is one in which only a well defined set of isolated frequencies are present. The radiation emitted by excited hydrogen atoms forms a line spectrum; the frequencies observed in the spectrum follow a simple mathematical relationship that involves small integers.

In 1913, Niels Bohr proposed a model of the hydrogen atom that explains its line spectrum. In this model, the energy of the hydrogen atom depends on the value of a number n, called the **quantum number**. The value of n must be a positive integer (1, 2, 3...), and each value of n corresponds to a different specific energy, E_n. The energy of the atom increases as n increases. The lowest energy is achieved for $n = 1$, this is called the **ground state** of the hydrogen atom. Other values of n correspond to **excited states** of the atom. Light is emitted when the electron drops from a higher energy state to a lower energy state; light must be absorbed to excite the electron from a lower energy state to a higher one. The frequency of light emitted or absorbed must be such that $h\nu$ equals the difference in energy between two allowed states of the atom.

De Broglie proposed that **matter, such as** electrons, should exhibit *wave-like properties*, this hypothesis of **matter waves** was proven experimentally by observing the diffraction of electrons. An object has a characteristic wavelength that depends on its **momentum** (mass times velocity, mv): $\lambda = \frac{h}{mv}$. Discovery of the wave properties of the electron led to **Heisenberg's uncertainty principle**, which states that *it is impossible to know both the exact momentum and the exact position of an electron simultaneously*.

3.2.2 Quantum Mechanics and Atomic Orbitals

In 1926, the Austrian physicist Erwin Schrödinger (1887 - 1961) proposed an equation, now known as *Schrödinger's wave equation*, that incorporates both the *wavelike and particle-like behavior* of the electron. His work opened a new way of dealing with subatomic particles known as **quantum mechanics** or **wave mechanics**. By solving the Schrödinger equation ($H\psi = E\psi$), we obtain a set of mathematical equations, called **wave functions** (ψ). Each allowed wave function has a precisely known energy, but the location of the electron cannot be determined exactly; rather, the probability of its being at a particular point in space is given by the *probability density*, ψ^2. The *electron density distribution* is a map of the probability of finding the electron at all points in space.

A wave function for an electron in an atom is called an **atomic orbital**; this atomic orbital describes a region of space in which there is a high probability of finding the electron. Energy changes within an atom are the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy (usually accompanied by the absorption or emission of a photon of light).

Each electron in an atom is described by four different **quantum numbers.** The first three (n, l, m_l) specify the particular orbital of interest, and the fourth (m_s) specifies how many electrons can occupy that orbital. The **principal quantum number**, n, is indicated by the integers 1, 2, 3... This quantum number specifies the energy of an electron and the size of the orbital (the distance from the nucleus of the peak in a radial probability distribution plot).

All orbitals that have the same value of n are said to be in the same *shell* (level). For a hydrogen atom with $n = 1$, the electron is in its *ground state*; if the electron is in the $n = 2$ orbital, it is in an *excited state*. The total number of orbitals for a given n value is n^2. The **azimuthal quantum number** (also known as the *angular quantum number* or *orbital quantum number*), l, is indicated by the letters s, p, d, f... corresponding to the values of 0, 1, 2, 3... The l quantum number specifies the shape of an orbital with a particular principal quantum number. For a given value of n, l can have integer values ranging from 0 to $n-1$. The azimuthal quantum number divides the shells into smaller groups of orbitals called **subshells** (sublevels). The **magnetic quantum number**, m_l, specifies the orientation in space of an orbital of a given energy (n) and shape (l). This number divides the subshell into individual orbitals which hold the electrons; there are $2l+1$ orbitals in each subshell. For a given value of l, m_l can have integral values ranging from $-l$ to l. *Cartesian labels* can be used to label the orientations of the orbitals. For example, the three $3p$ orbitals are designated $3p_x$, $3p_y$, and $3p_z$, with the subscripts indicating the axis along which the orbital is oriented. The **spin quantum number** (m_s): $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$, specifies the orientation of the spin axis of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).

The **Pauli exclusion principle** states that *no two electrons in the same atom can be in the same quantum numbers*. This principle places a limit of two on the number of electrons that can occupy any one atomic orbital. These two electrons differ in their value of m_s.

Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be *paired*. These substances are not attracted to magnets and are said to be **diamagnetic**. Atoms with more electrons that spin in one direction than another contain *unpaired* electrons. These substances are weakly attracted to magnets and are said to be **paramagnetic**.

3.2.3 Shapes of Atomic Orbitals

Contour representations are useful for visualizing the spatial characteristics (shapes) of the orbitals. An orbital with $l=0$ has a spherical shape with the nucleus at its center and is called an **s orbital**. In any atom, the size of the *s* orbital increases as *n* increases but the geometry remains spherical. Orbitals with $l=1$ are called ***p* orbitals**. Since the magnetic quantum number m_l can be -1, 0, or $+1$ when the value of the l is 1, *p* orbitals come in sets of three. The wave function for each *p* orbital has two *lobes* on opposite sides of the nucleus. They are oriented along the *x*-, *y*- and *z*-axes. Orbitals with $l=2$ are called ***d* orbitals**. Four of the *d* orbitals appear as shapes with four lobes around the nucleus; the fifth one, the $d_z{}^2$ orbital, is represented as two lobes along the z-axis and a "*doughnut*" in the *xy* plane. Regions in which the wave function is zero are called *node*s. There is zero probability that the electron will be found at a node. Orbitals with $l=3$ are called ***f* orbitals**. These orbitals are found only in the lanthanide and the actinide elements.

3.2.4 Electron Configurations

The distribution of electrons among the orbitals of an atom is called the **electron configuration**. The electrons are filled in according to a scheme known as the **Aufbau principle** ("building-up"), which corresponds (for the most part) to increasing energy of the subshells:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*

Another way to indicate the placement of electrons is an **orbital diagram**, in which each orbital is represented by a square (or circle), and the electrons as arrows pointing up or down (indicating the electron spin).

The ground-state electron configurations are generally obtained by placing the electrons in the atomic orbitals of lowest possible energy with the restriction that each orbital can hold no more than two electrons. When electrons occupy a subshell with more than one **degenerate orbital**, such as the 2*p* subshell, **Hund's Rule** states that *orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin*. For example, in the ground-state electron configuration of carbon, the two $2p$ electrons have the same spin and must occupy two different $2p$ orbitals.

The electrons in the outermost shell (the ones with the highest value of n) are the most energetic, and are the ones which are exposed to other atoms. This shell is known as the **valence shell**. The inner, **core electrons** (inner shell) do not usually play a role in chemical bonding. Elements with similar properties generally have similar outer shell configurations.

3.3 Periodicity of Atomic Properties

3.3.1 The Periodic Table of the Elements

The **periodic table** of the elements or just the periodic table is a tabular display of the chemical elements. Although precursors to this table exist, its invention is generally credited to the Russian chemist Dmitri Mendeleev in 1869, who discovered how to arrange the chemical elements in a table so that elements with similar chemical properties were in the same columns.

The layout of the table has been refined and extended over time, as new elements have been discovered, and the current standard table contains 118 elements as of March 2010 (elements 1 – 118). Elements are listed in order of increasing atomic number. Rows are arranged so that elements with similar properties fall into the same columns (*groups* or *families*). According to quantum mechanical theories of electron configuration within atoms, each row (*period*) in the table corresponded to the filling of a quantum shell of electrons.

A *group* (also known as a *family*) is a vertical column in the periodic table. There are 18 groups in the standard periodic table. In some groups, the elements have very similar properties and exhibit a clear trend in properties down the group. These groups tend to be given trivial (unsystematic) names, e.g. the **alkali metals** (group 1 except for hydrogen), **alkaline earth metals** (group 2), **halogens** (group 17), **pnictogens** (group 15), **chalcogens** (group 16), and **noble gases** (group 18). A *period* is a horizontal row in the periodic table. As one moves from left to right in a given period, the chemical properties of the elements slowly change. The periodic table can be divided into *s*, *p*, *d*, and *f* blocks. The *s*- and the *p*-blocks of elements in which the outermost subshell is an *s* or *p* subshell are called the **representative** (or **main-group**) **elements**. The elements in groups 1, 2 and 13 through 18 are main-group elements. The *d*-block elements in which a *d* subshell is being filled are called **transition elements** (or **transition metals**). The *f*-block elements are called the **inner transition elements**. The elements in which the 4*f* subshell is being filled are called the **lanthanide** elements. The **actinide** elements are those in which the 5*f* subshell is being filled. The lanthanide and the actinide elements are collectively referred to as the *f*-block metals.

3.3.2 Periodic Properties of the Elements

The properties of the elements exhibit trends. These trends can be predicted using the periodic table and can be explained and understood by analyzing the electron configurations of the elements. The elements in the same column of the periodic table have the same number of electrons in their valence orbitals. This similarity in valence electronic structure leads to the similarities among elements in the same group. The differences among elements in the same group arise because their valence orbitals are in different shells.

The **nuclear charge**, Z, is the charge of the nucleus. The magnitude of the *electrostatic attraction* between the electron and the nucleus is proportional to the magnitude of the charge of the nucleus. The **effective nuclear charge**, Z_{eff}, is the amount of positive charge on the nucleus perceived by an electron. Electrons intervening between the nucleus and an outer electron are said to **shield** or **screen** the outer electron from the nucleus so that the outer electron does not experience the full nuclear charge.

Elements tend to gain or lose valence electrons to achieve stable **octet** formation. In addition to this activity, there are two other important trends. First, electrons are added, one at a time, moving from left to right across a period. As this happens, the electrons of the outermost shell experience increasingly strong nuclear attraction, so the electrons become closer to the nucleus and more tightly bound to it. Second, moving down a column in the periodic table, the outermost electrons become less tightly bound to the nucleus. This happens because the number of filled principal energy levels (which shield the outermost electrons from attraction to the nucleus) increases downward within each group. These trends explain the periodicity observed in the elemental properties of **atomic radius**, **ionization energy**, **electron affinity**, and **electronegativity**.

1. Atomic Radius

The **atomic radius** of a chemical element is a measure of the size of its atoms, usually half of the distance between the centers of two atoms of that element that are just touching each other. Generally, the atomic radius decreases across a period from left to right and increases down a given group. The atoms with the largest atomic radii are located in Group I and at the bottom of groups.

Cations are smaller than their parent atoms; anions are larger than their parent atoms. For ions of the same charge, size increases going down a column of the periodic table. An *isoelectronic* series is a series of ions that has the same number of electrons. For such a series, size decreases with increasing nuclear charge as the electrons are attracted more strongly to the nucleus.

2. Ionization Energy

The **ionization energy**, or **ionization potential**, of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. The closer and more tightly bound an electron is to the nucleus, the more difficult it will be to remove, and the higher its ionization energy will be. The energy required to remove one electron is the **first ionization energy**, the **second ionization energy** is the energy required to remove a second valence electron. The second ionization energy is always greater than the first ionization energy. Ionization energies will increase going left to right across a period (decreasing atomic radius) and decrease going down a group (increasing atomic radius). Group 1 elements have low ionization energies because the loss of an electron forms a stable octet.

3. Electron Affinity

Electron affinity is the energy change that occurs when an electron is added to a gaseous atom. It reflects the ability of an atom to accept an electron to form an anion. Atoms with stronger effective nuclear charge have greater electron affinity. The more negative an electron affinity, the more stable the anion. The alkaline earths have low electron affinity values, however are relatively stable because of their filled s subshells. The halogens have high electron affinities because the adding one electron to an atom gives them an octet formation. The noble gases have electron affinities near zero, since each atom possesses a stable octet and will not accept an electron readily. Elements of other groups have low electron affinities. The elements in the upper right hand corner of the periodic table will have the highest electron affinity. The E.A. (electron affinity) number can be either positive or negative.

4. Electronegativity

When two elements are joined in a chemical bond, the element that attracts the shared electrons more strongly is more **electronegative**. Elements with low electronegativities (the metallic elements) are said to be **electropositive**. **Electronegativity** is a measure of the attraction of an atom for the electrons in a chemical bond. The higher the electronegativity of an atom, the greater its attraction for bonding electrons. Electronegativity is related to ionization energy. Electrons with low ionization energies have low electronegativities because their nuclei do not exert a strong attractive force on electrons. Elements with high ionization energies have high electronegativities due to the strong pull exerted on electrons by the nucleus. In a group, the electronegativity decreases as atomic number increases, as a result of increased distance between the valence electron and nucleus (greater atomic radius). An example of an electropositive (i.e. low electronegativity) element is caesium; an example of a highly electronegative element is fluorine.

The elements can be divided into categories: **metals**, **nonmetals**, and **metalloids**. Most elements are metals; they occupy the left side and the middle of the periodic table. Metals display several characteristic properties. For example, they are good conductors of heat and electricity and usually appear shiny. Metals are malleable and ductile. Except for mercury, which is a liquid, all metals are solids at room temperature. When metals react with nonmetals, the metal atoms are oxidized to cations and ionic compounds are generally formed. Most metal oxides are basic; they react with acids to form salts and water. Nonmetals appear in the upper-right section of the table. The properties of nonmetals are highly variable, but most nonmetals lack metallic luster and are poor conductors of heat and electricity. Several are gases at room temperature. Compounds composed entirely of nonmetals are generally molecular. Nonmetals usually form anions in their reactions with metals. Nonmetal oxides are acidic; they react with bases to form salts and water. Metalloids have properties that are intermediate between those of metals and nonmetals and they occupy a narrow band between the metals and nonmetals. The metalloids are dull-appearing, brittle solids at room temperature. The metalloids are sometimes called **semiconductors** because they conduct electricity better than nonmetals but not as well as metals. Silicon and germanium are widely used in the manufacture of semiconductor chips in the electronics industry. The tendency of an element to exhibit the properties of metals is called the **metallic character**. Metallic character is strongest for the elements in the leftmost part of the periodic table, and tends to decrease as we move to the right in any period (nonmetallic character increases with increasing ionization values). Within any group of elements (columns), the metallic character increases from top to bottom. This general trend is not necessarily observed with the transition metals.

The alkali metals (group 1A) are soft metals with low densities and low melting points. They have the lowest ionization energies of the elements. As a result, they are very reactive toward nonmetals, easily losing their outer *s* electron to form 1+ ions. The alkaline earth metals (group 2A) are harder and denser and have higher melting points than the alkali metals. They are also very reactive toward nonmetals, although not as reactive as the alkali metals. The alkaline earth metals readily lose their two outer s electrons to form 2+ ions. Both alkali and alkaline earth metals react with hydrogen to form ionic substances that contain the hydride ion, H^-.

Hydrogen is a nonmetal with properties that are distinct from any of the groups of the periodic table. It forms molecular compounds with other nonmetals, such as oxygen and the halogens.

Oxygen and sulfur are the most important elements m group 6A. Oxygen is usually found as a diatomic molecule, O_2 Ozone, O_3, is an important **allotrope** of oxygen. Oxygen has a strong tendency to gain electrons from other elements, thus oxidizing them. In combination with metals, oxygen is usually found as the oxide ion, O^{2-}, although salts of the *peroxide* ion, $O_2{}^{2-}$, and *superoxide* ion, $O_2{}^{-}$, are sometimes formed. Elemental sulfur is most commonly found as S_8 molecules. In combination with metals, it is most often found as the sulfide ion, S^{2-}.

The halogens (group 7A) are nonmetals that exist as diatomic molecules. The halogens have the most negative electron affinities of the elements. Thus their chemistry is dominated by a tendency to form 1− ions, reactions with metals.

The noble gases (group 8A) are nonmetals that exist as *monoatomic* gases. They are very unreactive because they have completely filled *s* and *p* subshells. Only the heaviest noble gases are known to form compounds, and they do so only with very active nonmetals, such as fluorine.

3.4 Basic Concepts of Chemical Bonding

Chemical bonds are interactions of electrons leading to strong forces of attraction which holds atoms together in molecules and compounds. The electrons that interact with each other are **valence electrons**, the ones that reside in the outermost electron shell of an atom. There are three general types of chemical bonds: **ionic**, **covalent**, and **metallic**.

Lewis dot symbols, or simply **Lewis symbols** (named for the American chemist G. N. Lewis), are ways of representing the number and the arrangement of valence electrons on an atom, ion, or molecule. Lewis symbols for single atoms are represented by the chemical symbol for that atom, surrounded by anywhere from zero to eight dots representing the number of valence electrons on the atom. The dots are placed on the four sides (top, right, bottom, left) of the element symbol. Each side can accommodate up to two electrons. If there are more than four, the electrons will group together in **electron pairs**, symbolized by placing two dots close together.

The tendencies of atoms to gain, lose, or share their valence electrons often follow the **octet rule**, which can be viewed as an attempt by atoms to achieve a stable noble-gas electron configuration. When several atoms join together to form molecular or ionic compounds, each atom generally achieves a full outer **octet** of electrons by bonding with one or more other atoms. These bonds are represented by lines instead of dots, with one line representing a single bond, two representing a double bond, etc. Pairs of electrons that form bonds are called **bonding pairs** or **shared pair**, and those that do not are called **lone pairs** or **unshared pair**.

In some situations, more than one Lewis structure is possible for a molecule. This occurs when a double or triple bond can be assigned to more than one pair of atoms, and the structures are called **resonance structures**. This can be indicated either by drawing all possible resonance structures, or drawing dashed rather than solid lines to indicate the different possible bonds.

An **ionic bond** is a type of chemical bond that involves a metal and a nonmetal ion (or polyatomic ions such as ammonium) through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions. Ionic compounds in the solid state form **lattice structures**. The two principal factors in determining the form of the lattice are the relative charges of the ions and their relative sizes. For a solid crystalline ionic compound the enthalpy change in forming the solid from gaseous ions is termed the **lattice energy**. Lattice energy increases with increasing charge on the ions and with decreasing distance between the ions. The experimental value for the lattice energy can be determined using the **Born-Haber cycle**.

A **covalent bond** results when two atoms share valence electrons between them. The most familiar examples of covalent bonding are seen in the interactions of nonmetallic elements with one another. The **bond order** is the number of electron pairs being shared between any two bonded atoms. A **single bond** has a bond order of one. A **double bond** consists of two bonding pairs, four electrons shared between two atoms, so the bond order is two. A **triple bond** consists of three bonding pairs; two atoms share six electrons, so the bond order is three. The strength of the bond depends on the magnitude of the mutual attraction between the bonded nuclei and the shared electrons.

The bond energy (BE) (also called **bond enthalpy** or **bond strength**) is the energy required to overcome this attraction. It is defined as the standard enthalpy change for breaking the bond in 1 mol of gaseous molecules. A covalent bond has a **bond length**, the distance between the nuclei of two bonded atoms. For a given pair of atoms, a higher bond order results in a shorter bond length and a higher bond energy. Some covalent substances, called **network covalent solids**, are held together by covalent bonds that extend in three dimensions throughout the sample.

In covalent bonds, the electrons may not necessarily be shared equally between two atoms. **Bond polarity** helps describe unequal sharing of electrons in a bond. In a **nonpolar covalent bond** the bonding electrons are equally shared by the two atoms. Whenever two atoms of the same element bond together, a nonpolar bond is formed. A **polar bond** is formed when electrons are unequally shared between two atoms. Polar covalent bonding occurs because one atom has a stronger affinity for electrons than the other (yet not enough to pull the electrons away completely and form an ion). The difference in the electronegativities of bonded atoms can be used to determine the polarity of a bond. The greater the difference, the more polar is the bond.

A molecule is composed of one or more chemical bonds (covalent bonds) between molecular orbitals of different atoms. Molecular compounds are either polar or nonpolar. Molecular polarity is dependent on the difference in electronegativity between atoms in a compound and the asymmetry of the compound's structure. Even though the total charge on a molecule is zero, a polar molecule has a positive side and a negative side. This separation of charge produces a **dipole**, the magnitude of which is given by the **dipole moment**, which is measured in debyes (D). Dipole moments increase with increasing amount of charge separated and increasing distance of separation. Any diatomic molecule X-Y in which X and Y have different electronegativities is a polar molecule. Molecules with mirror symmetry like oxygen, nitrogen, carbon dioxide, and carbon tetrachloride have no **permanent dipole moments**. Even if there is no permanent dipole moment, it is possible to induce a dipole moment by the application of an external **electric field**. This is called **polarization** and the magnitude of the dipole moment induced is a measure of

the polarizability of the molecular species.

Metallic bonds are formed when valence electrons of a metal are shared by every cations. In a metallic bond, bonding electrons are delocalized over a lattice of atoms. By contrast, in ionic compounds, the locations of the binding electrons and their charges are static. Because of delocalization or the free moving of electrons, it leads to the metallic properties such as conductivity, ductility and hardness.

3.5 Molecular Geometry and Bonding Theories

3.5.1 Valence-Shell Electron-Pair Repulsion (VSEPR) Theory and Molecular Shape

To construct the molecular shape from the Lewis structure, chemists employ **valence shell electron-pair repulsion** (VSEPR) theory. The premise of VSEPR is that the valence electron pairs surrounding an atom mutually repel each other, and will therefore adopt an arrangement that minimizes this repulsion, thus determining the **molecular geometry**, or **molecular shape**. The number of electron pairs surrounding an atom, both bonding and nonbonding, is called its **steric number** (SN). To accurately predict the shape of a small molecule we need to know the angles between the bonds in the compound. The **bond angle** (in degrees) is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom at the vertex.

Let's initially focus on molecules in which the central atom has no lone pairs. When there are two electron pairs ($SN = 2$) surrounding the central atom, their mutual repulsion is minimal when they lie at opposite poles of the sphere. This gives a **linear** arrangement, corresponding to a bond angle of 180°. For $SN = 3$, the bonding electron pairs all lie in a plane 120° apart in a **trigonal** planar arrangement, and for $SN = 4$, they are oriented 109.5° apart in a **tetrahedral** geometry. For $SN = 5$, two pairs reside on the north and the south poles of the sphere 180° apart, and three reside on the equator 120° apart. The resultant arrangement is called **trigonal bipyramidal**. Finally, for $SN = 6$, all the positions are equivalent. This arrangement defines an **octahe-**

dral molecular geometry.

Lone pairs of electrons are taken into account in determining the total coordination number and VSEPR geometry, but they are NOT used when defining the geometry of an atomic centre, only the atoms are used. Lone-pairs of electrons behave as if they are slightly bigger than bonded electron pairs and act to distort the geometry about the atomic centre so that bond angles are slightly *smaller* than expected. **Bent** (or **angular**), **trigonal pyramidal**, **see-saw**, **T-shaped**, **square pyramidal**, and **square planar** geometries result from different combinations of bonded atoms and lone pairs about a central atom. The observed bond angles in molecules deviate from the ideal values as a result of unequal repulsions between lone pairs and bonding pairs of electrons.

3.5.2 Valence Bond (VB) Theory and Orbital Hybridization

The VSEPR theory provides a simple means for predicting the shapes of molecules. However, it can not explain why bonds exist between atoms. The combination of Lewis's notion of electron-pair bonds to the idea of **atomic orbitals** leads to a model of chemical bonding called **valence-bond (VB) theory**. The basic principle of VB theory is that a covalent bond forms when the orbitals of two atoms **overlap** and are occupied by a pair of electrons that have the highest probability of being located between the nuclei. VB theory accounts for the observed shape (geometry) of a molecule by mixing, or *hybridizing*, atomic orbitals to create hybrid atomic orbitals. Mixing two *non-equivalent* orbitals of a central atom, one *s* and one *p*, gives rise to two *equivalent* ***sp*** **hybrid orbitals** that lie 180° apart. Overlap between two *sp* hybrid orbitals results in a **sigma** (σ) **bond** where the highest electron density lies along the bond axis with a linear orientation of valence electrons. Covalent bonds in which the electron density is greatest above and below, or in front of and behind, the bonding axis are called ***pi*** (π) **bonds**. Mixing one *s* and two *p* orbitals forms three sp^2 hybrid orbitals. Overlap between sp^2 orbitals and other atomic or hybrid orbitals results in up to three σ bonds and a trigonal planar orientation of valence electrons. Mixing one *s* and three *p* orbital forms four sp^3 **hybrid orbitals**. Overlap between sp^3 orbitals and other atomic or hybrid orbitals results in up to four σ bonds and a tetrahedral orientation of valence electrons. Mixing an *s* orbital, three *p* orbitals, and two *d* orbitals gives six equivalent sp^3d^2 **hybrid orbitals** that point toward the vertices of an octahedron. Overlap between sp^3d^2 orbitals and other atomic or hybrid orbitals results in up to six σ bonds. Mixing a 3*s* orbital, three 3*p* orbitals, and one 3*d* orbital yields five equivalent sp^3d **hybrid orbitals** with lobes that point toward the vertices of a trigonal bipyramid. Overlap between sp^3d **orbitals** and other atomic or hybrid orbitals results in up to five σbonds.

3.5.3 Molecular Orbital (MO) theory and electron delocalization

Molecular orbital (MO) theory is a second bonding theory based on the formation of **molecular orbitals** that belong to the molecule as a whole. Molecular orbital theory can provide a better description than valence bond theory of the location of unpaired electrons in molecules. MO theory explains the magnetic and the spectroscopic properties of molecules but does not help explain their shapes. Atomic orbitals with similar energies and shapes mix to give molecular orbitals delocalized over the entire molecule. Mixing two atomic orbitals creates a **bonding orbital** and an **antibonding orbital**. A bonding molecular orbital can contain a maximum of two electrons. A single covalent bond is formed when two electrons occupy a bonding molecular orbital. Whenever two atomic orbitals combine to form a bonding molecular orbital, a second higher energy antibonding orbital must also be formed. An antibonding molecular orbital can also contain a maximum of two electrons. Electrons in antibonding orbitals weaken the covalent bonds in a molecule. When the region of highest density in a bonding molecular orbital lies along the bond axis, the molecular orbital is designated as a **sigma (σ) molecular orbital**. Electrons in σ molecular orbitals form sigma (σ) bonds. Antibonding molecular orbitals that accompany sigma (σ) molecular orbitals are called σ^* (**"sigma star") molecular orbitals**. When the region of highest density in a bonding molecular orbital is not oriented along the bonding axis in a molecule, the molecular orbital is designated as a **pi (π) molecular orbital**. Electrons occupying π orbitals form π bonds. Antibonding molecular orbitals that accompany π molecular orbitals are called π^* (**"pi star") molecular orbitals.**

The bond order in a molecular orbital description of a molecule or ion equals one-half the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A **molecular orbital diagram** shows the relative energies of the molecular orbitals of a molecule including all σ, σ^*, π and π^* molecular orbitals. Each molecular orbital can be occupied by a maximum of two electrons. We can write electron configurations of molecules using the designations σ, σ^*, π and π^* to describe the type of molecular orbitals occupied by electrons, subscripts to identify the atomic orbitals that led to the MOs and superscripts to identify the number of electrons in each molecular orbital; for example, $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ for N_2.

3.5.4 Intermolecular Forces

All matter is held together by force. **Intramolecular forces** (bonding forces) exist within each molecule (or polyatomic ion) and influence the chemical properties of the substance. **Intermolecular forces** exist between the molecules (or ions) and influence the physical properties of the substance. Intermolecular forces are much weaker than bonding (intramolecular) forces.

There are several types of intermolecular forces: ion-dipole, dipole-dipole, hydrogen bonding, and dispersion forces. When an ion and a nearby polar molecule (dipole) attract each other, an **ion-dipole** force results. Ion-dipole forces are important in solutions of ionic compounds in polar solvents (e.g. a salt in aqueous solvent). The ions become separated because the attractions between the ions and the oppositely charged poles of the H_2O molecules overcome the attractions between the ions themselves. A **dipole-dipole force** exists between neutral, but polar molecules. Polar molecules attract one another when the partial positive charge on one molecule is near the partial negative charge on the other molecule. The polar molecules must be in close proximity for the dipole-dipole forces to be significant. Dipole-dipole forces are characteristically weaker than ion-dipole forces. Dipole-dipole forces increase with an increase in the polarity of the molecule. **Hydrogen bonding** is a special type of dipole-dipole interactions occurring between polar covalent molecules that possess a hydrogen atom bonded to an extremely electronegative element, specifically N, O, and F. **Dispersion forces** (or **London forces**) are the intermolecular forces that exist between nonpolar atoms or molecules. They result from the movement of the electrons in the molecule which generates temporary positive and negative regions (instantaneous dipole moments) in the molecule. **Van der Waals' forces** include all intermolecular forces that act between electrically neutral molecules. The stronger the van der Waals forces, the higher the boiling points and heats of vaporization and fusion. The **van der Waals radius** determines the shortest distance over which intermolecular forces operate; it is always larger than the covalent radius.

3.6 Chemical Reactions

A **chemical reaction** is a process that leads to the transformation of one set of chemical substances to another. The substance(s) initially involved in a chemical reaction are called **reactants**. Chemical reactions are usually characterized by a chemical change, and they yield one or more **products**, which usually have properties different from the reactants. Chemical reactions tend to involve the motion of electrons, leading to the formation and the breaking of chemical bonds.

3.6.1 Reaction Types

There are many different types of chemical reactions and more than one way of classifying them. Some common reaction types are listed below:

(1) **Direct Combination** or **Synthesis** reaction, in which two or more chemical elements or compounds combine to form a more complex product.

$$A + B \rightarrow AB$$

$$S\,(s) + O_2(g) \rightarrow SO_2(g)$$

(2) **Chemical Decomposition** or **Analysis** Reaction, in which a compound is decomposed into smaller compounds or elements.

$$AB \rightarrow A + B$$

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

(3) **Single Displacement** or **Substitution** Reaction, characterized by an element being displaced out of a compound by a more reactive element.

$$A + BC \rightarrow AC + B$$

$$Zn\ (s) + CuSO_4(aq) \rightarrow Cu\ (s) + ZnSO_4(aq)$$

(4) **Metathesis** or **Double Displacement** Reaction, in which two compounds exchange ions or bonds to form different compounds.

$$AB + CD \rightarrow AD + CB$$

$$CaCl_2(aq) + 2AgNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2AgCl\ (s)$$

(5) **Acid-base** Reactions, broadly characterized as reactions between an acid and a base, can have different definitions depending on the acid-base concept employed.

$$HBr + NaOH \rightarrow NaBr + H_2O$$

(6) **Oxidation-reduction** (**Redox**) Reaction describes all chemical reactions in which the *oxidation number* (*oxidation state*) of a participating chemical species changes. Most redox processes involve the transfer of oxygen atoms, hydrogen atoms, or electrons, with all three processes sharing two important characteristics: (1)they are coupled—i.e. in any oxidation reaction a reciprocal reduction occurs, and (2) they involve a characteristic net chemical change—i.e. an atom or electron goes from one unit of matter to another. An example of a redox reaction is:

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

in which I_2 is reduced to I^- and $S_2O_3^{2-}$ (thiosulfate anion) is oxidized to $S_4O_6^{2-}$.

The **oxidation number** of an element indicates the number of electrons lost, gained, or shared as a result of chemical bonding. Substances that have the ability to oxidize other substances are said to be oxidative and are known as **oxidizing agents**, **oxidants**, or **oxidizers**. Oxidants are usually chemical elements or substances with elements in high oxidation numbers or highly electronegative substances/elements that can gain one or two extra electrons by oxidizing an element or substance. Substances that have the ability to reduce other substances are said to be reductive and are known as **reducing agents**, **reductants**, or **reducers**.

(7) **Combustion** Reaction, a kind of redox reaction in which any combus-

tible substance combines with an oxidizing element, usually oxygen, to form oxidized products and generate heat (*exothermic* reaction). The term combustion is usually used for only large-scale oxidation of whole molecules, i.e. a controlled oxidation of a single functional group is not combustion. Usually in a combustion reaction oxygen combines with another compound to form carbon dioxide and water.

$$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$$

$$CH_2S + 6F_2 \rightarrow CF_4 + 2HF + SF_6$$

(8) **Isomerization** Reaction, in which a chemical compound undergoes a structural rearrangement without any change in its net atomic composition.

(9) **Disproportionation** Reaction, a redox reaction in which one reactant forming two distinct products varying in oxidation state.

$$2Sn^{2+} \rightarrow Sn + Sn^{4+}$$

(10) **Hydrolysis** Reaction , in which water is one of the reactants, and a larger molecule is split into two smaller molecules, one of which has the hydrogen from the water and the other has the OH group from the water. Hydrolysis is actually a special type of substitution reaction. The general form for a hydrolysis reaction is:

$$X^-(aq) + H_2O(l) \leftrightarrow HX(aq) + OH^-(aq)$$

3.6.2 Writing Chemical Equations

A **chemical equation** is a symbolic, or shorthand, way of representing of a chemical reaction where the reactant entities are given on the left side and the product entities on the right side. The equation identifies the reactants and the products, the formulas of the participants, the phases of the participants (solid, liquid, gas), and the amount of each substance. The **law of conservation of mass** dictates the quantity of each element does not change in a chemical reaction. Thus, each side of the chemical equation must have an equal number of atoms. Similarly, the charge is conserved in a chemical reaction. This is the **law of conservation of charge**. Therefore, the same charge must be present on both sides of the balanced equation.

For example, in the industrial synthesis of ammonia, the reactants N_2 and H_2 react to produce NH_3. The balanced chemical equation is:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

All balanced chemical equations have the following features:

(1) In a chemical equation, formulas for the reactants are written on the left side of the equation and formulas for the products are written on the right. The two sides of the equation are joined by an arrow (→) or equal sign (=). The arrow indicates the direction of reaction.

(2) An integer precedes the formula of each substance. These numbers are the *stoichiometric coefficients*. When no number appears (as for N_2 in this equation), the stoichiometric coefficient is 1.

(3) The stoichiometric coefficients in a chemical equation are the smallest integers that give a balanced equation.

(4) Charge is conserved. In this equation, all participants are neutral species, so charge is conserved regardless of the stoichiometric coefficients.

3.6.3 Writing Equations for Aqueous Ionic Reactions

Many reactions take place in aqueous solution, and many of those involve ions. Chemists use three types of equations to represent aqueous ionic reactions: molecular, total ionic, and net ionic equations.

A **molecular equation** is a balanced chemical equation in which ionic compounds are written as neutral formulas rather than as ions. For example,

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

An **ionic equation** is a chemical equation in which electrolytes are written as dissociated ions. Ionic equations are used for single and double displacement reactions that occur in aqueous solutions. The **total ionic equation** shows all the soluble ionic substances dissociated into ions. For example,

$$Ca^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + 2AgCl(s)$$

Notice that the $Ca^{2+}(aq)$ and $NO_3^-(aq)$ ions are unchanged and are present on both sides of the equation. Since they are not undergoing chemical reaction, they can be referred to as **spectator ions**. These ions are present as part of the reactants to balance the charge. If we subtract the spectator ions from each side of the equation, we then have a **net ionic equation**. The net ionic equation for the above reaction is:

$$2Cl^-(aq) + 2Ag^+(aq) \rightarrow 2AgCl(s)$$

or, in reduced balanced form,

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

3.6.4 Yields of Chemical Reactions

When chemical reactions are performed under practical conditions, the amounts of products obtained are almost always less than the amounts predicted by stoichiometric analysis. The amount of a product obtained from a reaction is often reported as a **yield**. The amount of product predicted by stoichiometry is the **theoretical yield**, whereas the amount actually obtained is the **actual yield**. The **percent yield** is the percentage of the theoretical amount that is actually obtained.

3.7 The Behavior of Gases

Some elements, e.g. O_2, N_2 and H_2, exist as gases under ordinary conditions of temperature and pressure. Many molecular compounds are also gases. Substances that are liquids or solids under ordinary conditions can usually exist in the gaseous state, too, where they are often referred to as **vapors**.

Gases behave differently from the other two commonly studied states of matter, solids and liquids. Gases have neither fixed volume nor shape; gas volume changes greatly with pressure and temperature; gases flow much more freely than liquids and solids; most gases have relatively low densities under normal conditions; and gases are miscible.

3.7.1 Gas Laws

Experiments with a large number of gases reveal that four variables are needed to define the physical condition, or state, of a gas: pressure (p), volume (V), temperature (T), and amount (number of moles, n). The equations that express the relationships among T, p, V and n are known as the **gas laws**. Three key relationships exist among the four gas variables are: Boyle's, Charles's and Avogadro's laws. Each of these gas laws expresses the effect of one variable on another, with the remaining two variables held constant.

The Pressure-Volume Relationship – **Boyle's Law**, which states that the volume of definite quantity of gas maintained at constant temperature is inversely proportional to the pressure. The Temperature-Volume Relationship— **Charles's Law**, which can be stated as the volume occupied by any sample of gas at a constant pressure is directly proportional to the absolute temperature (in kelvins). The Quantity-Volume Relationship— **Avogadro's Law**, which states that the volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles (or molecules) present in the container. The conditions 0 ℃ and 1 atm are referred to as the **standard temperature and pressure** (**STP**). The **molar volume** of a gas at STP is 22.4 L.

The **ideal gas law** is a combination of all the gas laws. The ideal gas law can be expressed as $pV = nRT$. This equation is known as the **ideal-gas equation**. An **ideal gas** is a hypothetical gas whose pressure, volume, and temperature behavior is completely described by the ideal-gas equation. The term R in the ideal-gas equation is a **proportionality constant** known as the universal **gas constant**. The value and units of R depend on the units of p, V, n and T. Temperature must always be expressed as an absolute temperature.

The pressure exerted by a particular component of a mixture of gases is called the **partial pressure** of that gas. **Dalton's law of partial pressures** states that the pressure of a mixture of gases simply is the sum of the partial pressures of the individual components. The **mole fraction** is the ratio of the moles of one component of a mixture to the total moles of all components. The partial pressure of a component of a mixture is equal to its mole fraction times the total pressure.

3.7.2 Kinetic-Molecular Theory

The gas laws are based upon empirical observations and describe the behavior of a gas in macroscopic terms. An alternative approach to understanding the behavior of a gas is to begin with the atomic theory. In principle, the observable properties of gas (pressure, volume, temperature) are the consequence of the actions of the molecules making up the gas. The **Kinetic Molecular Theory** of Gases begins with five postulates that describe the behavior of molecules in a gas:

(1)Gases consist of large numbers of molecules (or atoms, in the case of the noble gases) that are in *continuous*, *random* motion.

(2)The volume of the molecules of the gas is *negligible* compared to the total volume in which the gas is contained.

(3) *Attractive* and *repulsive* forces between gas molecules are negligible.

(4) Collisions between molecules are perfectly *elastic*. Energy can be transferred between molecules during collisions, but the *average kinetic energy* of the molecules does not change with time, as long as the temperature of the gas remains constant.

(5)The average kinetic energy of the molecules is proportional to the absolute temperature. At any given temperature the molecules of all gases have the same average kinetic energy.

The kinetic-molecular theory explains both pressure and temperature at the molecular level. The pressure of a gas is manifested at the boundary of the vessel it is confined in, and is caused by collisions of the molecules of the gas with the walls of the container. The magnitude of the pressure is related to how hard and how often the molecules strike the wall. The "hardness" of the impact of the molecules with the wall will be related to the velocity of the molecules times the mass of the molecules. The absolute temperature of a gas is a measure of the average kinetic energy of its molecules. If two different gases are at the same temperature, their molecules have the same average kinetic energy. If the temperature of a gas is doubled, the average kinetic energy of its molecules is doubled.

Although the molecules in a sample of gas have an average kinetic energy (and therefore an average speed), the individual molecules move at various speeds. Collisions change individual molecular speeds but the distribution of speeds remains the same. Their speeds are distributed over a wide range; the distribution varies with the molar mass of the gas and with temperature. At the same temperature, lighter gases move, on average, faster than heavier gases. At higher temperatures a greater fraction of the molecules are moving at higher speeds. The **root-mean-square** (rms) speed, u, varies in proportion to the square root of the absolute temperature and inversely with the square root of the molar mass: $u = \sqrt{3RT/M}$. The average kinetic energy of the gas molecules, ε, is related directly to u^2. $\varepsilon = \frac{1}{2}mu^2$. The *rms* speed for a given speed distribution is greater in magnitude than the **most probable speed** or the **mean speed**.

3.7.3 Molecular Effusion and Diffusion

Effusion is the escape of gas molecules through a tiny pore or pinhole into an evacuated space. The effusion rate is inversely proportional to the square root of its molar mass (**Graham's law**). **Diffusion** is the spontaneous intermingling (mixing) of dissimilar gases (fluids) that are initially spatially separated. The average distance traveled by a molecule between collisions with another molecule is called the **mean free path**. Because molecules undergo frequent collisions with one another, the **mean free path** is short. Collisions between molecules limit the rate at which a gas molecule can diffuse.

3.7.4 Real Gases

Real gases depart from ideal behavior because the molecules possess finite volume and because the molecules experience attractive forces for one another upon collision. In 1873, Johannes van der Waals realized the limitations of the ideal gas law and proposed an equation that accounts for intrinsic molecular volume and intermolecular forces of **real gases**. The **van der Waals equation** for n moles of a real gas is:

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

where a and b are van der Waals constants, experimentally determined positive numbers specific for a given gas.

3.8 Aqueous Reactions and Solution Stoichiometry

3.8.1 Solution Formation

Many of the chemical reactions that take place within us and around us involve substances dissolved in water. Solutions in which water is the dissolving medium are called **aqueous solutions**.

A **solution** is a homogeneous mixture of two or more substances. At least two substances must be mixed in order to have a solution. The substance present in greater quantity is usually called the **solvent**. The other substances in the solution are known as the **solutes**; they are said to be dissolved in the solvent. In most common instances water is the solvent. The gases, liquids, or solids dissolved in water are the solutes.

3.8.2 Electrolyte

An ionic compound that conducts electricity in molten (fused) or aqueous (solution) state can be classified as an **electrolyte**. Compound composed of molecules that does not conduct electricity when molten or in aqueous solutions is called a **non-electrolyte**. There are two categories of electrolytes, strong electrolytes and weak electrolytes, which differ in the extent to which they conduct electricity. **Strong electrolytes** are those solutes that exist in solution completely or nearly completely as ions. Essentially all soluble ionic compounds (such as NaCl) and a few molecular compounds (such as HCl) are strong electrolytes. **Weak electrolytes** are those solutes that exist in solution mostly in the form of molecules with only a small fraction in the form of ions. Polar covalent compounds are typically weak electrolytes. For example, in a solution of acetic acid (CH_3COOH) most of the solute is present as CH_3COOH molecules. Only a small fraction (about 1%) of the CH_3COOH is present as H^+ (*aq*) and CH_3COO^- (*aq*) ions. When representing the ionization of a weak electrolyte in solution, a double arrow is used, indicating that the forward and the reverse reactions can achieve a chemical balance called a **chemical equilibrium**.

3.8.3 Concentrations of Solutions

There are a number of ways to express the relative amounts of solute and solvent in a solution. Scientists use the term **concentration** to designate the amount of solute dissolved in a given quantity of solvent or solution.

Percent composition (by mass) is the ratio parts of solute to one hundred parts of solution and is expressed as a percent. **Molarity** describes the concentration of a solution in moles of solute divided by liters of solution. Masses of solute must first be converted to moles using the molar mass of the solute.

This is the most widely used unit for concentration when preparing solutions in chemistry and biology. The units of molarity, mol · L^{-1}, are usually represented by a symbol "M". **Molality** describes the number of moles of solute dissolved in exactly one kilogram of solvent. **Grams per liter** represent the mass of solute divided by the volume of solution, in liters. This measure of concentration is most often used when discussing the solubility of a solid in solution. The **mole fraction**, X, of a component in a solution is the ratio of the number of moles of that component to the total number of moles of all components in the solution. **Parts per million** (**ppm**), is a ratio of parts of solute to one million parts of solution, and is usually applied to very dilute solutions.

Many laboratory chemicals such as acids are purchased as **concentrated** solutions (stock solutions). Solutions of lower concentrations can then be obtained by adding water, a process called **dilution**.

3.8.4 Precipitation Reactions

Reactions that result in the formation of an insoluble product are known as **precipitation reactions**. A **precipitate** is an insoluble solid formed by a reaction in solution. Precipitation reactions occur when certain pairs of oppositely charged ions attract each other so strongly that they form an insoluble ionic solid.

The **solubility** of a substance is the amount of that substance that can be dissolved in a given quantity of solvent. Any substance with a solubility less than 0.01 mol · L^{-1} will be referred to as **insoluble**.

3.8.5 Titrations

Titration is the quantitative measurement of an **analyte** in solution by completely reacting it with a reagent solution. The reagent is called the **titrant** and must either be prepared from a **primary standard** or be standardized versus a primary standard to know its exact concentration. The point in the titration at which stoichiometrically equivalent quantities of reactants are brought together is called the **equivalence point**. The number of moles of analyte is calculated from the volume of reagent that is required to react with all of the analyte, the titrant concentration, and the reaction stoichiometry. The equivalence point is often determined by visual an **indicator** that is also present in the solution. For acid-base titrations, indicators are available that change color when the pH changes. When all of the analyte is neutralized, further addition of the titrant causes the pH of the solution to change causing the color of the indicator to change.

3.9 Chemical Equilibrium

3.9.1 The Concept of Equilibrium

In stoichiometry calculations, the reactions are assumed to run to completion. In fact, however, many reactions do not go to completion but rather approach an equilibrium state in which both reactants and products are present. In a chemical process, **chemical equilibrium** is the state in which the chemical activities or concentrations of the reactants and the products have no net change with time. Usually, this would be the state that results when the *forward* and the *reverse* processes are occurring at the same rate. This process is called **dynamic equilibrium**. If the equilibrium state is one in which significant quantities of both reactants and products are present, then the reaction is said to *incomplete* or *reversible*.

3.9.2 Properties of Equilibrium Constants

In 1864, two Norwegian chemists, Guldberg and Waage, observed that at a given temperature, a chemical system reaches a state in which a particular ratio of reactant and product concentrations has a constant value. This is one way of stating the **law of chemical equilibrium**, or the **law of mass action**. For the general equilibrium equation of the form $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$, the **equilibrium constant expression** is written as follows:

$$K_{eq} = \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b} \text{ for a gas-phase equilibrium}$$

$$K_{eq} = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \text{ for an aqueous equilibrium}$$

The equilibrium-constant expression depends only on the stoichiometry of the reaction. For a system at equilibrium at a given temperature, K_{eq} will be a constant called the **equilibrium constant**. A large value of K_{eq} implies that there are more products than reactants and that the equilibrium lies to the right. A small K_{eq} value implies there are more reactants than products and the reaction lies to the left. K_{eq} changes only with temperature.

Equilibria for which all substances are in the same phase are called **homogeneous equilibria**. An equilibrium involving more than one phase is said to be **heterogeneous**. Because the concentrations of pure solids and liquids are constant, these substances are left out of the equilibrium-constant expression for a heterogeneous equilibrium.

The **reaction quotient**, Q, is the same as the equilibrium constant expression, but for partial pressures or concentrations of the reactants and products before the system reaches equilibrium. If the system is at equilibrium, $Q = K_{eq}$. If $Q \neq K_{eq}$, however, the system is not at equilibrium. When $Q < K_{eq}$, the reaction will move toward equilibrium by forming more products (the reaction moves from left to right); when $Q > K_{eq}$, the reaction will proceed from right to left. Knowing the value of K_{eq} makes it possible to calculate the equilibrium amounts of reactants and products, often by the solution of an equation in which the unknown is the change in a partial pressure or concentration.

3.9.3 Le Châtelier's principle

Le Châtelier's principle states that if a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a component, there will be a tendency for a net reaction in the direction that reduces the effect of this change. By this principle, whenever the concentration of a component changes, the equilibrium system reacts to consume some of the added substance or produce some of the removed substance. The effects of changing the pressure or volume of a reaction can be similarly deduced. The enthalpy change for a reaction indicates how an increase in temperature affects the equilibrium. A temperature increase favors the endothermic direction, and a temperature decrease favors the exothermic direction. Catalysts affect the speed at which equilibrium is reached but do not affect the magnitude of K_{eq}.

3.10 Thermochemistry

All changes in matter, whether chemical or physical, are accompanied by changes in the energy content of the matter. **Thermodynamics** is the study of heat and its transformations. **Thermochemistry** is the branch of thermodynamics that deals with the heat involved in chemical reactions.

All energy is either potential or kinetic. An object has **potential energy** by virtue of its position and **kinetic energy** by virtue of its motion.

A thermodynamic **system** is anything that we want to describe and study by itself. Once we select something as a system, everything outside the system is its **surroundings**. A system is separated from its surroundings by a **boundary**, across which matter and/or energy can be transferred. A system may be open, closed, or isolated, depending on what kinds of transfers take place. An *open system* exchanges matter and energy with its surroundings. A *closed system* exchanges energy but not matter, and an *isolated system* exchanges neither matter nor energy with the surroundings. The conditions that describe a system are collectively called its **state**. Conditions that must be specified to establish the state of a system are called **state variables**. The state variables for chemical systems are familiar quantities: pressure (p), volume (V), temperature (T), and amounts of substances (n). A property that depends only on the state of the system is called a **state function**. A property that depends on how a change takes place is called a **path function**.

When energy is transferred from one object to another, it appears in two forms, heat and work. **Heat** (or thermal energy, symbol Q) is the energy transferred between a system and its surroundings as a result of a difference in their temperatures only. All other forms of energy transfer (mechanical, electrical, etc) involve some type of **work** (W), the energy transferred when an object is moved by force. In thermodynamics we define **energy** as the capacity to do work or to transfer heat.

The **internal energy**, E (some texts use the symbol U), of a system is the sum of all the kinetic and the potential energies of its component parts. The internal energy of a system can change because of energy transferred between the system and the surroundings. Energy is neither created nor destroyed but only changes form (transforms). The **first law of thermodynamics**, which is also called the **law of conservation of energy**, states that the change in the internal energy of a system (ΔE), is the sum of the heat (Q) and the work (W): $\Delta E = Q + W$. The internal energy E, is a **state function**. Both Q and W are not state functions and they have a sign that indicates the direction of energy transfer. When heat is transferred from the surroundings to the system, $Q > 0$. Likewise, when the surroundings do work on the system, $W > 0$. In an **endothermic** process the system absorbs heat from the surroundings; in an **exothermic** process the system releases heat to the surroundings.

When a gas is produced or consumed in a chemical reaction occurring at constant pressure, the system may perform **pressure-volume work** against the prevailing pressure. For this reason, we define a new state function called **enthalpy**, H, which is a thermodynamic quantity equal to the internal energy of a system plus the product of its volume and pressure. In systems where only pressure-volume work due to gases is involved, the change in the enthalpy of a system, ΔH, equals the heat gained or lost by the system at constant pressure. For an endothermic process, $\Delta H > 0$; for an exothermic process, $\Delta H < 0$.

Every substance has a characteristic enthalpy. In a chemical process, the **enthalpy of reaction** is the enthalpy of the products minus the enthalpy of the reactants: $\Delta H_{rxn} = H(\text{products}) - H(\text{reactants})$. Enthalpies of reaction follow some simple rules: (1)Enthalpy is an extensive property, so the enthalpy of reaction is proportional to the amount of reactant that reacts. (2)Reversing a reaction changes the sign of ΔH. (3)The enthalpy of reaction depends on the physical states of the reactants and the products.

The amount of heat transferred between the system and the surroundings is measured experimentally by **calorimetry**. A **calorimeter** is a device used to measure heat changes that accompany physical or chemical processes. The **heat capacity** C of a substance is the amount of heat required to change its temperature by one degree, and has units of energy per degree. The heat capacity for 1 mol of a pure substance is called its **molar heat capacity**; for 1 g of the substance, we use the term **specific heat**. Water has a very high specific heat, $4.18\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$. The amount of heat, Q, absorbed by a substance is the product of its specific heat, its mass, and its temperature change: $Q =$ (specific heat) × (grams of substance) × ΔT.

If a calorimetry experiment is carried out under a constant pressure, the heat transferred provides a direct measure of the enthalpy change of the reaction. *Constant-volume calorimetry* is carried out in a vessel of fixed volume called a **bomb calorimeter**. Bomb calorimeters are used to measure the heat evolved in combustion reactions. The heat transferred under constant-volume conditions is equal to ΔE. However, corrections can be applied to ΔE values to yield enthalpies of combustion.

Because enthalpy is a state function, ΔH depends only on the initial and final states of the system. Thus, the enthalpy change of a process is the same whether the process is carried out in one step or in a series of steps. **Hess's law** states that the enthalpy change for any overall process is equal to the sum of enthalpy changes for any set of steps that leads from the reactants to the products. We can therefore calculate ΔH for any process, as long as we can write the process as a series of steps for which ΔH is known.

The **enthalpy of formation**, ΔH_f, of a substance is the enthalpy change for the reaction in which the substance is formed from its constituent elements. The **standard enthalpy** of a reaction, ΔH°, is the enthalpy change when all reactants and products are under standard conditions, which are defined to be 1 atm pressure and 298 K (25 ℃). Combining these ideas, the **standard enthalpy of formation**, ΔH_f°, of a substance is the enthalpy change accompanying the formation of one mole of a chemical substance from pure elements in their most stable forms under standard conditions. For any element in its most stable state at 298 K and 1 atm pressure, $\Delta H_f^\circ = 0$. The standard enthalpy change for any reaction can be readily calculated from the standard enthalpies of formation of the reactants and products in the reaction:

$$\Delta H^\circ_{rxn} = \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants})$$

When substances move from one phase to another, energy is released or absorbed because of changes in intermolecular forces. The **molar heat of solution** (ΔH_{soln}) measures the net energy flow that occurs as a substance dissolves. The molar energy change resulting from the dilution is called the **heat of dilution**. The heat needed to melt one mole of a substance at its normal melting point is called the **molar heat of fusion** (ΔH_{fus}). The heat needed to vaporize one mole of a substance at its normal boiling point is called the **molar heat of vaporization** (ΔH_{vap}).

3.11 Acid-Base Equilibria

Acids and bases have been known by their properties since the early days of experimental chemistry. For example, acids turn litmus red, whereas bases turn litmus blue. There are several different definitions of acids and bases, and the most common ones are Arrhenius, Brønsted-Lowry and Lewis definitions.

3.11.1 Arrhenius Acids and Bases

One of the first definitions of acids and bases was suggested by Arrhenius. An **Arrhenius acid** is a substance that increases the concentration of the hydrogen ion, H^+ (*aq*), when dissolved in water. Note that chemists often write H^+ (*aq*) and refer to the hydrogen ion when describing acid-base reactions but the free hydrogen nucleus, a proton, does not exist alone in water, it exists as the **hydronium** ion, H_3O^+ (*aq*). An **Arrhenius base** is a molecule which increases the concentration of the hydroxide ion when dissolved in water. Ionic hydroxide compounds such as NaOH, KOH, and $Ca(OH)_2$ are among the most common bases. Because of the equilibrium in water, increasing the concentration of one of these ions decreases the concentration of the other.

When a solution of an acid and that of a base are mixed, a **neutralization reaction** occurs. In general, a neutralization reaction between an acid and a metal hydroxide produces water and a **salt.**

3.11.2 Brønsted-Lowry Acids and Bases

The Brønsted-Lowry concept of acids and bases is more general than the

Arrhenius concept and emphasizes the transfer of a proton (H^+) from an acid to a base. According to Brønsted-Lowry definition, a **Brønsted-Lowry acid** is a substance that can donate a proton, and a **Brønsted-Lowry base** is a substance that can accept a proton. An acid-base reaction is, thus, the removal of a hydrogen ion from the acid and its addition to the base. Water is an **amphoteric** substance, one that can function as both a Brønsted-Lowry acid and a base, depending on the substance with which it reacts. The removal of a proton (hydrogen ion) from a Brønsted-Lowry acid produces its **conjugate base**, which is the acid with a hydrogen ion removed, and the reception of a proton by a Brønsted-Lowry base produces its **conjugate acid**, which is the base with a hydrogen ion added. Together, an acid and its conjugate base (or a base and its conjugate acid) are called a **conjugate acid-base pair**.

Water itself dissociates into ions, H^+ (*aq*) and OH^- (*aq*), very slightly in an equilibrium process known as **autoionization** (or self-ionization). The extent of this autoionization is expressed by the **ion-product constant** for water:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} (25\ ℃)$$

This relationship describes both pure water and aqueous solutions. The K_w expression indicates that the product of $[H^+]$ and $[OH^-]$ is a constant. Thus, as $[H^+]$ increases, $[OH^-]$ decreases. In an acidic solution, $[H^+] > [OH^-]$; in a basic solution, $[H^+] < [OH^-]$; and in a neutral solution, $[H^+] = [OH^-]$.

The **acidity** or **basicity** of something, therefore, can be measured by its hydrogen ion concentration. **pH** is a logarithmic measure of the **acidity** (or **basicity**) of an aqueous solution. By definition, $pH = -\log [H^+]$. At 25 ℃ the pH of a neutral solution is 7.00, whereas the pH of an acidic solution is below 7.00, and the pH of a basic solution is above 7.00. The pH value of a solution can be measured with a pH meter, or it can be estimated using acid-base indicators. The pX notation is also used to represent the negative log of other small quantities, as in pOH and pK_w.

The strength of an acid refers to its ability or tendency to lose a proton. A **strong acid** is a strong electrolyte that completely dissociates in water; in other words, one mole of a strong acid HA dissolves in water yielding one mole of H^+ and one mole of the conjugate base, A^-. The common strong acids are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$ and H_2SO_4. **Superacids** are acids stronger than 100% sulfuric acid. In contrast a **weak acid** is weak electrolyte that only partially dissociates and at equilibrium both the acid and the conjugate base are in solution. The extent of ionization is expressed by the **acid-dissociation constant**, K_a, which is the equilibrium constant for the reaction $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$. Stronger acids have a higher K_a and a lower pK_a than weaker acids. The **degree of ionization** of a weak acid (HA) is the ratio of $[A^-]$ to the initial (total) acid concentration and is usually expressed as a percentage.

Molecules of different acids can ionize to form different numbers of $H^+(aq)$ ions. Both HCl and HNO_3 are **monoprotic** acids, which yield one $H^+(aq)$ per molecule of acid. **Polyprotic** acids yield two or more $H^+(aq)$ per molecule of acid. Sulfuric acid (H_2SO_4) is a **diprotic** acid, and phosphoric acid (H_3PO_4) is a **triprotic** acid. These polyprotic acids have acid-dissociation constants that decrease in magnitude in the order $K_{a1} > K_{a2} > K_{a3}$.

Weak bases include NH_3, amines, and the anions of weak acids. The extent to which a weak base reacts with water to generate the corresponding conjugate acid and $OH^-(aq)$ is measured by the **base-dissociation constant**, K_b. The relationship between the strength of an acid and the strength of its conjugate base is expressed quantitatively by the equation $K_a \times K_b = K_w$, where K_a and K_b are dissociation constants for conjugate acid-base pairs.

A salt is an ionic compound formed by the reaction of an acid and a base. The acid-base properties of salts can be ascribed to the behavior of their respective cations and anions. The ions may react with water in a **hydrolysis** reaction to produce $H^+(aq)$ or $OH^-(aq)$ and hence affect the pH of a solution. **Hydrolysis** is a general term for the splitting of a water molecule. The conjugate base of a weak acid will hydrolyze, as will the conjugate acid of a weak base. If K_b for the anion is greater than K_a for the cation, the solution is basic. If K_b for the anion is less than K_a for the cation, the solution is acidic. If K_a and K_b are similar, the solution is close to neutral.

Oxoacids have the general formula HOX where X can be any atom and may or may not share bonds to other atoms. The electronegativity of the central atom (E) and the number of O atoms determine oxoacid acidity. With the same central atom E, acid strength increases as the number of oxygen attached to E increases. With the same number of oxygens around E, acid strength increases with the electronegativity of E. **Carboxylic acids** are organic acids that contain an acidic hydroxyl group and a carbonyl (C=O bond).

Strong acids (or strong bases) dissociate completely to yield H_3O^+ (or OH^-) in water; in effect, water equalizes (levels) their strengths. The term **leveling effect** refers to a solvent's ability to level the effect of a strong acid or base dissolved in it. Strong bases are **leveling solvents** for acids, weak bases are **differentiating solvents** for acids.

3.11.3 Lewis Acids and Bases

The Lewis concept of acids and bases emphasizes the shared electron pair rather than the proton. A **Lewis acid** is any species that accepts an electron pair, and a **Lewis base** is any species that donates an electron pair. The product of any Lewis acid-base reaction is called an **adduct**, a single species that contains a new covalent bond. The Lewis concept is more general than the Brønsted-Lowry concept because it greatly expands the classes of acids. Many species that do not contain H in their formula can function as Lewis acids by accepting an electron pair in their reactions. Molecules with polar double bonds act as Lewis acids, as do those with electron-deficient atoms. Metal ions act as Lewis acids when they dissolve in water, which acts as a Lewis base, to form a hydrated cation.

3.12 Additional Aspects of Aqueous Equilibria

The phenomenon of lowering the degree of ionization of a weak electrolyte by adding a solution of a strong electrolyte having a common ion is called **common-ion effect**. In other words, the presence of a common ion suppresses the ionization of a weak acid or a weak base.

A **buffer solution** is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. It has the property that the pH of the solution changes very little when a small amount of strong acid or base is added to it. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. The **buffer capacity** of a solution is the amount of added H_3O^+ or OH^- the buffer solution can tolerate without exceeding a specified pH range. **Buffer range** is the pH range over which a buffer effectively neutralizes added acids or bases. The relationship between the pH of a buffer solution, pK_a, and the concentrations of the weak acid and its conjugate base can be expressed by the **Henderson-Hasselbalch** (H-H) equation:

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

An **acid-base titration** is the determination of the concentration of an acid or base by exactly neutralizing the acid/base with an acid or base of known concentration. The plot of the pH of an acid (or base) as a function of the volume of added base (or acid) is called a **pH titration curve**. A **pH indicator** is a weak acid or base that has a color that is different from that of its conjugate base or acid. The titration curve of a strong acid-strong base titration exhibits a large change in pH in the immediate vicinity of the **equivalence point**. For strong acid-weak base or weak acid-strong base titrations, the pH change in the vicinity of the equivalence point is not as large.

A **solubility equilibrium** exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound. The equilibrium is an example of dynamic and heterogeneous equilibrium in that some individual molecules migrate between the solid and solution phases such that the rates of dissolution and precipitation are equal to one another. The **solubility-product constant** (or simply the **solubility product**), K_{sp}, is an equilibrium constant that expresses quantitatively the extent to which the compound dissolves. The K_{sp} is equal to the product of the concentrations of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation. The value of K_{sp} can be obtained from the solubility, and vice versa. Substances that have $K_{sp} << 1$ are classified as **insoluble**. Salts that have K_{sp} between 10^{-2} and 10^{-5} are **slightly soluble**, and solids which have $K_{sp} > 10^{-2}$ are **soluble**. The solubility of a slightly soluble substance can be decreased by the presence of a common ion. The solubility of compounds containing basic anions increases as pH decreases. Salts with anions of negligible basicity (the anions of strong acids) are unaffected by pH changes.

A **complex ion** is formed when two or more negatively charges or neutral Lewis bases (ligands) attach themselves to a central metal ion in solution. The extent to which such complex formation occurs is expressed quantitatively by the **formation constant** (K_f) for the complex ion. A hydrated metal ion is a complex ion with water molecules as ligands. Other ligands can displace the water molecules attached to the metal ion in a stepwise process. A ligand increases the solubility of a slightly soluble ionic compound if it forms a complex ion with the cation. **Amphoteric metal hydroxides** dissolve very little in water but to a much greater extent in both acidic and basic solutions due to acid-base reactions that form soluble complex ions.

An interesting application of solubility equilibrium is the **selective precipitation** of ions, which is a useful way to separate and detect the presence of metal ions in mixtures. Ions are precipitated selectively by adding a precipitating ion until the K_{sp} of one compound is exceeded as much as possible without exceeding the K_{sp} of the other. An extension of this approach is to control the equilibrium of the slightly soluble compound by simultaneously controlling an equilibrium system that contains the precipitating ion. The **qualitative analysis** of metal ions in solution can be carried out by separating the ions into groups on the basis of precipitation reactions and then analyzing each group for individual metal ions.

3.13 Chemistry of Coordination Compounds

3.13.1 Metal Complexes

A **metal complex** or merely **complex** is a structure consisting of a central atom or ion (usually metallic), bonded to a surrounding array of molecules or anions. If the complex carries a net charge, it is generally called a **complex ion**. Compounds that contain complexes are called **coordination compounds**. The ions or molecules surrounding the central metal atom in a complex are called **ligands** (from the Latin word *ligare*, meaning "to bind"). Ligands are normally either anions or polar molecules. Every ligand has at least one unshared pair of valence electrons. The atom within a ligand that is directly bonded to the central atom or ion is called the **donor atom**. The central atom or ion, together with all ligands form the **coordination sphere**.

A coordination complex is the product of a Lewis acid-base reaction in which ligands bond to a central metal atom (or ion) by **coordinate covalent bonds** (donating electrons from a lone electron pair into an empty metal orbital). Because ligands contain at least one pair of electrons to donate to a metal atom/ion, they can function as Lewis bases (electron-pair donors). Ligands are also called **complexing agents**. Metal atoms/ions (particularly transition-metal ions) have empty valence orbitals, so they can act as Lewis acids (electron-pair acceptors).

Coordination compounds and complexes are distinct chemical species that have physical and chemical properties and behaviors different from the metal atom/ion and ligands from which they are composed. Complex formation can also significantly change other properties of metal ions, such as their ease of oxidation or reduction. Hydrated metal ions are actually complex ions in which the ligand is water.

The charge of a complex is the sum of the charges on the central metal and on its surrounding ligands. The **coordination number** is the number of donor atoms bonded to the central metal atom/ion.

3.13.2 Ligands with More than One Donor Atom

Where a ligand is bound to a metal ion through a single donor atom, as with NH_3 and Cl^-, the ligand is said to be **monodentate** or **unidentate** (from the Latin, meaning "one-toothed"). Where two donor atoms can be used to bind to a metal ion, as with ethylenediamine ($H_2NCH_2CH_2NH_2$), the ligand is said to be **bidentate**, and where several donor atoms are present in a single ligand as with ethylenediaminetetraacetate ion, abbreviated $[EDTA]^{4-}$, the ligand is said to be **polydentate**. Because bi- or polydentate ligand appear to grasp the metal between two or more donor atoms, they are also known as **chelating agents** (from the Greek word *chele* for "claw"). The generally larger formation constants for polydentate ligands as compared with the corresponding monodentate ligands is known as the **chelate effect**.

The molecular geometry of a complex depends on the coordination number and nature of the metal ion. The most common coordination number is six, and almost all metal complexes with coordination number 6 adopt *octahedral* geometry. A coordination number of four is also common, it gives rise to either of two geometries - *square planar* or *tetrahedral*. A complex ion whose metal ion has a coordination number of 2 is *linear*. There are many cases which deviate from a regular geometry, due to the use of ligands of different types, the size of ligands, or electronic effects.

3.13.3 Isomerism in Coordination Compounds

Isomers are compounds with the same chemical formula but different arrangements of atoms and therefore different properties. There exist many kinds of **isomerism** in coordination complexes. **Structural isomers** differ in the bonding arrangements of the ligands. One simple form of structural isomerism, known as **linkage isomerism**, occurs with **ambidentate** ligands which are capable of coordinating in more than one way. For example, NO_2 is an ambidentate ligand; it can bind to a metal at either the N atom or at an O atom. **Coordination isomers** occur when the composition of the complex ion changes but not that of the compound. One way this type of isomerism occurs is when ligand and counter ion exchange positions. **Stereoisomers** are isomers with the same chemical bonding arrangements but different spatial arrangements of ligands. The most common forms of stereoisomerism are **geometric isomerism** and **optical isomerism**. Geometric isomers differ from one another in the relative locations of donor atoms in the coordination sphere; the most common are *cis-trans* isomers. Optical isomerism occurs when the mirror image of a compound is not superimposable with the original compound.

3.13.4 Crystal-Field Theory

Many of the properties of metal complexes are dictated by their electronic structures. The **crystal-field theory** successfully accounts for many properties of coordination compounds, including their color and magnetism. The crystal field model explains that the properties of complexes result from the splitting of *d*-orbital energies, which arises from electrostatic interactions between metal ion and ligands. For an octahedral complex, the *d* orbitals are split into a lower-energy set of three degenerate orbitals (the t_{2g} set) and a higher-energy set of two degenerate orbitals (the e_g set). The splitting of orbital energies is called the **crystal field effect**, and the difference in energy between the e_g and the t_{2g} sets of orbitals is the **crystal field splitting energy** (Δ). Different ligands create crystal fields of different strength and, thus, cause the *d*-orbital energies to split to different extents. **Strong-field ligands** lead to a larger splitting energy; **weak-field ligands** lead to a smaller splitting energy. Visible light can cause a ***d-d* transition**, in which an electron is excited from a lower-energy *d* orbital to a higher-energy *d* orbital. The **spectrochemical series** lists ligands in order of their ability to split the *d*-orbital energies in octahedral complexes. Strong-field ligands create a splitting of *d*-orbital energies that is large enough to overcome the **spin-pairing energy**. The *d* electrons then preferentially pair up in the lower-energy orbitals, producing a **low-spin complex**. When the ligands exert a weak crystal field, the splitting of the *d* orbitals is small. The electrons then occupy the higher-energy *d* orbitals in preference to pairing up in the lower-energy set, producing a **high-spin complex**.

The crystal-field model also applies to tetrahedral and square-planar complexes, which leads to different *d*-orbital splitting patterns. In a tetrahedral crystal field, the splitting of the *d* orbitals is exactly opposite that of the octahedral case. The splitting by a tetrahedral crystal field is much smaller than that of an octahedral crystal field, so tetrahedral complexes are always high-spin complexes.

Coordination compounds play important roles in nature. Among the most important chelating agents in nature are those derived from the *porphine* molecule. Complexes derived from porphine are called *porphyrins*. Different porphyrins contain different metal ions and have different substituent groups attached to the carbon atoms at the ligand's periphery. *Chlorophyll*, which is involved in photosynthesis in plants, is a coordination complex of Mg(Ⅱ). *Hemoglobin*, the oxygen transporter in the human body, is a coordination complex of Fe(Ⅱ).

3.14 Nuclear Chemistry

Nuclear chemistry is the subfield of chemistry dealing with radioactivity, nuclear processes and nuclear properties. **Radiochemistry** is the chemistry of radioactive materials. It includes the production of radionuclides and their compounds by processing irradiated materials or naturally occurring radioactive materials, the application of chemical techniques to nuclear studies, and the application of radioactivity to the investigation of chemical, biochemical or biomedical problems. **Radiation chemistry** is the study of the chemical effects of radiation on matter; this is very different to radiochemistry as no radioactivity needs to be present in the material which is being chemically changed by the radiation.

An atom consists of an extremely small, positively charged **nucleus** surrounded by a cloud of negatively charged electrons. Nuclei consist of positively charged **protons** and electrically neutral **neutrons**, both of which are called **nucleons**. Each particular type of nucleus is called a **nuclide**. Nuclides are characterized by the number of protons (Z) and neutrons (N) that they possess. Two nuclides of an element with different numbers of neutrons are **isotopes**. The **mass number** of a nuclide, A, is its total number of protons and neutrons. Unstable nuclides decompose spontaneously into other, more stable nuclides. These decompositions are called **nuclear decay**, and unstable nuclides are called **radioactive**. These radioactive nuclei are called **radionuclides**, and the atoms containing them are called **radioisotopes**.

Two positively charged particles repel each other, yet many nuclides with more than one proton are extremely stable. This stability arises from a nucleon-nucleon attraction called the **strong** or **nuclear force**. This force is about 100 times stronger than proton-proton repulsion, but it operates only at the very small distances inside the nucleus. Because of this strong force, neutrons and protons are bound tightly in the nucleus.

When a radionuclide decays, it forms a nuclide of lower energy, and the excess energy is carried off by the emitted radiation. The decaying, or reactant, nuclide is called the **parent**; the product nuclide is called the **daughter**.

In nuclear equations, reactant and product nuclei are represented by giving their mass numbers and atomic numbers, as well as their chemical symbol. The total Z (charge, number of protons) and the total A (sum of protons and neutrons) of the reactants equal those of the products:

$$^{\text{Total } A}_{\text{Total } Z}\text{Reactants} = ^{\text{Total } A}_{\text{Total } Z}\text{Products}$$

There are five common kinds of radioactive decay: emission of alpha particles (α decay), emission of beta particles (β decay), positron emission (positron decay), electron capture, and emission of gamma radiation (γ decay).

Positrons have the mass of an electron but carry a positive charge and so are examples of **antimatter**. When a particle of matter encounters a particle of antimatter, both particles are converted into energy (they annihilate one another) yielding gamma (γ) rays.

Radioactive decay follows first-order kinetics. The decay rate, or **activity** (A), of a radioactive sample is the change in number of nuclei (N) divided by the change in time (t). The SI unit for the activity of a radioactive source is the **becquerel (Bq)**, defined as one nuclear disintegration per second. A related unit is the **curie** ($1\ \text{Ci} = 3.70 \times 10^{10}\ \text{Bq}$). **Geiger counters** and **scintillation counters** count the emissions from radioactive samples. **Half-life** ($t_{1/2}$) is the time required for one half of the atoms in any starting sample of a radioisotope to decay. Radionuclides have constant half-lives, and some can therefore be used to date objects. For example, **radiocarbon dating** involves measuring the amount of radioactive ^{14}C that remains in an object derived from plant or animal tissue to calculate the age of the object.

The energy produced in nuclear reactions is accompanied by measurable losses of mass in accordance with Einstein's relationship, $\Delta E = \Delta m\ c^2$. The difference between the mass of the nucleus and the masses of the individual nucleons that make up the nucleus is known as the **mass defect**. The mass defect of a nuclide makes it possible to calculate its **nuclear binding energy**, the energy required to separate the nucleus into individual nucleons. **Binding energy per nucleon** is a measure of the relative stability of a nucleus.

The neutron-to-proton ratio is an important factor determining nuclear stability. Stable nuclei have neutron-to-proton ratios that fall within a range of values that form the **belt of stability**. Unstable nuclides undergo radioactive decay. In general, neutron-rich (mass number greater than the average atomic mass) nuclides undergo β decay; neutron-poor nuclides undergo positron emission or electron capture. Nuclei with 2, 8, 20, 28, 50, or 82 protons, or 2, 8, 20, 28, 50, 82, or 126 neutrons, are generally more stable than nuclei that do not contain these numbers of nucleons. These numbers of protons and neutrons are called **magic numbers**. Nuclei with even numbers of both protons and neutrons are generally more stable than those with odd numbers of nucleons. A nuclide may undergo a series of decay steps before a stable nuclide forms. This series of steps is called a **radioactive series**, or a **nuclear disintegration series**.

Nuclear transmutation, an artificial method of transforming one nucleus into another, can be brought about by bombarding nuclei with either high speed charged particles or neutrons. Artificial nuclides including radioactive transuranium elements ($Z > 92$) are produced in **linear accelerators** and **cyclotrons**, where atoms and subatomic particles collide at high speeds. Uranium-235, uranium-233, and plutonium-239 undergo **nuclear fission** when they capture a neutron. Nuclear fission is a nuclear reaction in which the nucleus of an atom splits into lighter nuclei, often producing free neutrons and photons (in the form of gamma rays), as well. The resulting nuclear reaction is a **nuclear chain reaction**, a reaction in which the neutrons produced in one fission cause further fission reactions. Chain reactions require a minimum or **critical mass** of a fissionable isotope. Nuclear fission produces energy for **nuclear power** and to drive explosion of **nuclear weapons**. A **breeder reactor** is used to make ^{239}Pu from ^{235}U while also producing energy to make electricity. **Nuclear fusion** requires high temperatures because nuclei must have large kinetic energies to overcome their mutual repulsions. They are therefore called **thermo-nuclear reactions**. It is not yet possible to generate a controlled fusion process.

Alpha particles, β particles, positrons, and γ rays have enough energy to remove tightly bound electrons from the orbital of an atom, causing the atom to become charged or ionized. **Ionizing radiation** can cause tissue damage and molecular changes in DNA. The amount of energy deposited in matter (especially living tissue) by radiation is called the **absorbed dose**. The **gray**

(Gy), with units $J \cdot kg^{-1}$, is the SI unit of absorbed dose, which represents the amount of radiation required to deposit 1 joule of energy in 1 kilogram of any kind of matter. The **rad** is a smaller unit; 100 rads = 1 Gy. Equal doses of different types or energies of radiation cause different amounts of damage to living tissue. Therefore the **equivalent dose** was defined to give an approximate measure of the biological effect of radiation. An **equivalent dose** of ionizing radiation is the product of the energy absorbed and the relative biological effectiveness (RBE) of the radiation; it is expressed in **sieverts** (Sv) and **rems**, 100 rems = 1 Sv. Alpha (α) particles have a larger RBE than β particles and γ rays but have the least penetrating power.

Selected radioactive isotopes are useful as tracers in the human body to map biological activity and diagnose diseases. Other radionuclides are used to treat cancers using external sources or internally through injections or implants.

References

[1] McNaught A D, Wilkinson A. Compendium of chemical terminology: second edition (the "Gold Book") [M]. Oxford: Blackwell Scientific Publications, 1997.

[2] Silberberg M S. Chemistry: The molecular nature of matter and change: third edition [M]. New York: McGraw Hill Company, 2003.

[3] Gilbert T R, Kirss R V, Foster N, Davies G. Chemistry: second edition [M]. New York: W. W. Norton & Company Inc., 2009.

[4] Petrucci R H, Harwood W S, Herring F G. General chemistry: principles and modern applications: eighth edition [M]. New Jersey: Prentice - Hall, Inc., 2002.

[5] Brown T L, LeMay Jr H E, Bursten B E, Burdge J R. Chemistry: the central science: ninth edition [M]. New Jersey: Pearson Education, Inc., 2003.

[6] Oxtoby D W, Freeman W A, Block T F. Chemistry: science of change: fourth edition [M]. California: Brooks/Cole - Thomson Learning, 2003.

[7] Olmsted III J, Williams G M. Chemistry: third edition [M]. New York: John Wiley & Sons, Inc., 2002.

[8] http://physics.info/light/.

[9] http://www.merriam-webster.com/dictionary/.

[10] http://www.thefreedictionary.com/.

[11] http://en.wikipedia.org/wiki/.

[12] http://www.angelo.edu/faculty/kboudrea/general/quantum_numbers/Quantum_Numbers.htm.

[13] http://www.3rd1000.com/chem301/chem301b.htm.

[14] http://library.thinkquest.org/3659/structures/shapes.html.

[15] http://www.chemguide.co.uk/atoms/properties/atomorbs.html.

[16] http://chemistry.about.com/od/periodictableelements/a/periodictrends.htm.

[17] http://ce.t.soka.ac.jp/chem/iwanami/intorduct/ch05periodic.pdf.

[18] http://www.newworldencyclopedia.org/entry/Periodic_table.

[19] http://www.chem1.com/acad/webtext/atoms/atpt-6.html.

[20] http://www.chemguide.co.uk/physmenu.html#top.

[21] http://www.chem.uwimona.edu.jm:1104/courses/IC10Kiso.html.

[22] http://goldbook.iupac.org/.

[23] http://misterguch.brinkster.net/6typesofchemicalrxn.html.

[24] http://www.sky-web.net/science/reaction-types.htm.

[25] http://en.wikibooks.org/wiki/General_Chemistry/Types_of_chemical_reactions.

[26] http://www.course-notes.org/chemistry/topic_notes/basic_concepts_of_chemical_bonding.

[27] http://www.meta-synthesis.com/webbook/45_vsepr/VSEPR.html.

[28] *http://www.chem.purdue.edu/gchelp/vsepr/.*

[29] http://winter.group.shef.ac.uk/vsepr/.

[30] http://cost.georgiasouthern.edu/chemistry/general/molecule/vsepr.htm.

[31] http://www.science.uwaterloo.ca/~cchieh/cact/c120/hybrid.html.

[32] http://www.britannica.com/EBchecked/topic/621929/valence-bond-theory.

[33] http://www.chemistryexplained.com/Te-Va/Valence-Bond-Theory.html.

[34] http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/.

[35] http://www.chem.qmul.ac.uk/software/download/mo/.

[36] http://www.chem.ufl.edu/~itl/2045/lectures/lec_g.html.

[37] http://antoine.frostburg.edu/chem/senese/101/liquids/faq/h-bonding-vs-london-forces.shtml.

[38] http://www.mikeblaber.org/oldwine/chm1045/notes/Gases/Diffuse/Gases09.htm.

[39] http://www.chem.ufl.edu/~itl/2045/lectures/lec_d.html.

[40] http://www.mikeblaber.org/oldwine/chm1045/notes/Gases/Kinetic/Gases08.htm.

[41] http://en.wikipedia.org/wiki/Kinetic_theory.

[42] http://premedicaluniversity.com/mcat-general-chemistry-podcast/.

[43] http://www.answers.com/topic/electrolyte.

[44] http://www.tutorvista.com/content/chemistry/chemistry-ii/electrolysis/electrolytes-

and-nonelectrolytes.php.
[45] http://www.chem.purdue.edu/gchelp/howtosolveit/Solutions/concentrations.html.
[46] http://chemistry.about.com/od/lecturenotesl3/a/concentration.htm.
[47] http://www.drmechalke.com/chem1035/chapter_4cont/precipitaion.pdf.
[48] http://www.files.chem.vt.edu/chem-ed/titration/titratn.html.
[49] http://www.chem1.com/acad/webtext/chemeq/.
[50] http://www.shodor.org/unchem/advanced/equ/index.html.
[51] http://www.answers.com/topic/chemical-equilibrium.
[52] http://www.encyclopedia.com/topic/Thermochemistry.aspx.
[53] http://www.answers.com/topic/thermochemistry.
[54] http://www.chem1.com/acad/webtext/energetics/CE02.html.
[55] http://www.chemguide.co.uk/physical/acideqiamenu.html.
[56] http://en.wikipedia.org/wiki/Acid%E2%80%93base_reaction.
[57] http://www.chem.purdue.edu/gchelp/cchem/.
[58] http://www.public.asu.edu/~jpbirk/CHM-115_BLB/Chpt24/index.htm.
[59] http://www.science.uwaterloo.ca/~cchieh/cact/applychem/coordcpd.html.
[60] http://www.docstoc.com/docs/26811777/Coordination-Compounds.
[61] http://www.chemistryexplained.com/Co-Di/Coordination-Compounds.html.
[62] http://wwwchem.uwimona.edu.jm/courses/IC10Kiso.html.
[63] http://en.wikipedia.org/wiki/Coordination_complex.
[64] http://en.wikipedia.org/wiki/Crystal_field_theory.
[65] http://wapedia.mobi/en/Nuclear_chemistry.
[66] http://en.wikipedia.org/wiki/Nuclear_chemistry.

Chapter 4 Nomenclature of Organic Compounds

Nomenclature in organic chemistry is of two types: **common** (or "trivial") and **systematic**. Some common names existed long before organic chemistry became an organized branch of chemical science. Methane, ethane, propane, toluene, aniline, and anisole are common names. There are over 16 million known organic compounds which can't all have simple names (common names), and no one would remember them if they did. To establish an international standard of naming organic compounds to facilitate communication, the **IUPAC** (International Union of Pure and Applied Chemistry) have developed systematic nomenclature, a set of rules for naming organic compounds based on their structures that allows any compound to be given a unique name that can be deduced directly from its chemical structure. Conversely, a chemical structure can be deduced from its systematic name. The goal of the system is to give each structure a unique and unambiguous name, and to correlate each name with a unique and unambiguous structure.

IUPAC nomenclature is based on naming a molecule's longest chain of carbons connected by single bonds, whether in a continuous chain or in a ring. All deviations, either multiple bonds or atoms other than carbon and hydrogen, are indicated by prefixes or suffixes according to a specific set of priorities.

Organic compounds are classified into families that contain *functional groups*. The IUPAC rules assign names to organic compounds consist of three parts: *prefix*, *parent*, and *suffix*. The prefix lists the substituents and their position, the parent gives the number of carbon atoms in the longest continuous carbon atom chain, and the suffix identifies the family.

4.1 Naming Acyclic Alkanes

Alkanes are one family of organic compounds. Alkanes are not considered a functional group as they are relatively unreactive and do not undergo many chemical reactions.

Acyclic (noncyclic) alkanes are classified into two subgroups: **straight** or **unbranched chains** and **branched chains**. Unbranched alkanes are also called *normal alkanes*. The names of the first four members of the homologous series of unbranched are retained names. Methane, ethane, propane, and butane are retained for CH_4, CH_3CH_3, $CH_3CH_2CH_3$, and $CH_3CH_2CH_2CH_3$, respectively. They were coined more than 100 years ago. There are no alternative names for them. Thereafter, the number of carbon atoms in the chain is specified by a multiplicative prefix of the series **penta-**, **hexa-**, etc. of Table 4.1 preceding the suffix **-ane**, which identifies the compound as a member of the alkane family. The letter "**a**", which ends the name of the multiplicative prefix, is elided.

Table 4.1 Numerical prefixes

1 Mono	11 Undeca	21 Henicosa	53 Tripentaconta
2 Di	12 Dodeca	22 Docosa	54 Tetrapentaconta
3 Tri	13 Trideca	23 Tricosa	55 Pentapentaconta
4 Tetra	14 Tetradeca	30 Triaconta	56 Hexapentaconta
5 Penta	15 Pentadeca	31 Hentriaconta	57 Heptapentaconta
6 Hexa	16 Hexadeca	35 Pentatriaconta	60 Hexaconta
7 Hepta	17 Heptadeca	40 Tetraconta	70 Heptaconta
8 Octa	18 Octadeca	48 Octatetraconta	80 Octaconta
9 Nona	19 Nonadeca	50 Pentaconta	90 Nonaconta
10 Deca	20 Icosa	52 Dopentaconta	100 Hecta

Examples:

hex (a) + ane = hexane $CH_3-[CH_2]_4-CH_3$

hexa + dec(a) + ane = hexadecane $CH_3-[CH_2]_{14}-CH_3$

The IUPAC rules assign names to unbranched alkanes as shown in Table 4.2.

Table 4.2 IUPAC Names of Unbranched Alkanes

Number of carbons	Molecular formula	Name	Number of carbons	Molecular formula	Name
1	CH_4	Methane	16	$C_{16}H_{34}$	Hexadecane
2	C_2H_6	Ethane	17	$C_{17}H_{36}$	Heptadecane
3	C_3H_8	Propane	18	$C_{18}H_{38}$	Octadecane
4	C_4H_{10}	Butane	19	$C_{19}H_{40}$	Nonadecane
5	C_5H_{12}	Pentane	20	$C_{20}H_{42}$	Icosane
6	C_6H_{14}	Hexane	21	$C_{21}H_{44}$	Henicosane
7	C_7H_{16}	Heptane	22	$C_{22}H_{46}$	Docosane
8	C_8H_{18}	Octane	23	$C_{23}H_{48}$	Tricosane
9	C_9H_{20}	Nonane	24	$C_{24}H_{50}$	Tetracosane
10	$C_{10}H_{22}$	Decane	30	$C_{30}H_{62}$	Triacontane
11	$C_{11}H_{24}$	Undecane	31	$C_{31}H_{64}$	Hentriacontane
12	$C_{12}H_{26}$	Dodecane	32	$C_{32}H_{66}$	Dotriacontane
13	$C_{13}H_{28}$	Tridecane	40	$C_{40}H_{82}$	Tetracontane
14	$C_{14}H_{30}$	Tetradecane	50	$C_{50}H_{102}$	Pentacontane
15	$C_{15}H_{32}$	Pentadecane	100	$C_{100}H_{202}$	Hectane

An **alkyl** substituent can be considered as an alkane from which one hydrogen has been removed; the name is derived by replacing the suffix **-ane** with **-yl**. Thus, CH_3- is a methyl group, CH_3CH_2- an ethyl group, and so forth.

Alkyl groups with more than two carbons are often designated by common rather than IUPAC names. Some alkyl groups and their common names:

$CH_3CH_2CH_2-$	*n*-propyl	$(CH_3)_2CH-$	isopropyl
$CH_3CH_2CH_2CH_2-$	*n*-butyl	$(CH_3)_2CH-CH_2-$	isobutyl
$CH_3-CH_2-CH(CH_3)-$	*s*-butyl	$(CH_3)_3C-$	*t*-butyl
$CH_3CH_2CH_2CH_2CH-$	*n*-pentyl	$(CH_3)_2CH-CH_2-CH_2-$	isopentyl
$CH_3-CH_2-C(CH_3)_2-$	*t*-pentyl	$(CH_3)_3C-CH_2-$	neopentyl

The prefix ***n*-** (normal) refers to a straight-chain alkyl group. The prefix **iso-** describes an alkyl group in which a carbon bonded to a hydrogen and CH_3 two groups—that occurs in isobutane has come to be called "**iso.**" Here, ***s*-** is short for "**secondary**", *t*- means "**tertiary**". The structural unit with a carbon surrounded by four other carbons is called "***neo***." Substituents that contain hyphens in their name, such as ***n***-, *s*(**ec**)-, and *t*(**ert**)-, are named alphabetically by the parent substituent, not ***n***, ***s***, or ***t***. Substituents containing prefixes "**iso**" and "**neo**", with no following hyphen, are alphabetized by "***i***" and "***n***".

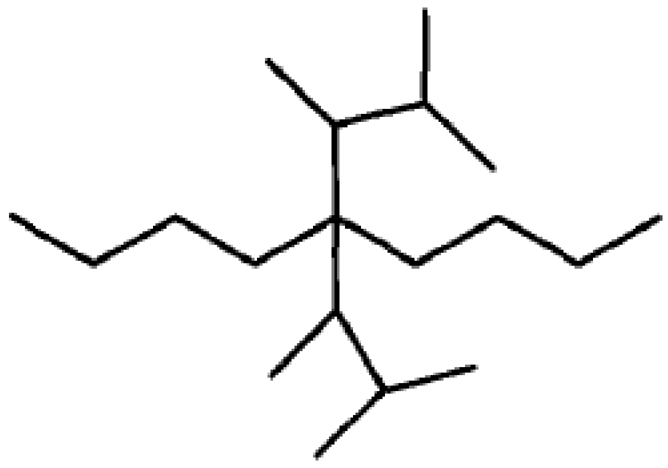
Branched-chain alkanes can be considered to be constituted of a principal chain and side-chains. They are named by using a precise set of operations:

(1) Select the longest continuous chain of carbon atoms, and use the name of this chain as the base name of the compound. When there are two longest chains of equal length, use the chain with the greater number of substituents as the main chain.

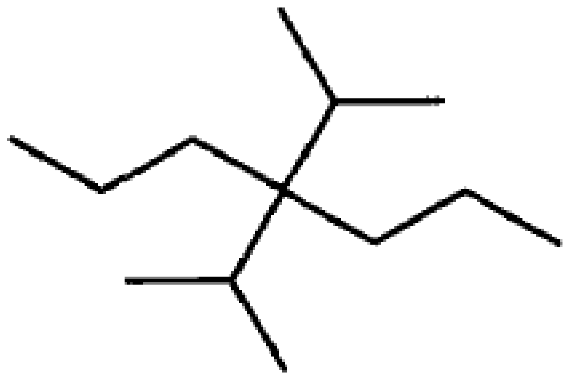
(2)Number each carbon atom in the parent chain from the end nearest the branch point. Determination of the position of side-chains named as alkyl substituents on the principal chain. Substituents are given the lowest combination of numbers.

(3)Identification and naming each alkyl substituent which will be treated as prefixes. Preceding the name by the number of the carbon atom to which it is attached.

(4)If a structure has identical substituents, then the prefixes **di-**, **tri-**, **tetra-**, etc are used to represent the number of substituents with the names of simple substituents and retained names. Different or modified prefixes are used with complex substituents: **bis-**, **tris-**, **tetrakis- pentakis-**, **hexakis-**, etc. It is alphabetized as the substituent, not by **di**, **tri**, or **tetra**. Each substituent requires a number and commas separate the numbers.



5,5—bis (1,2-dimethylpropyl) nonane

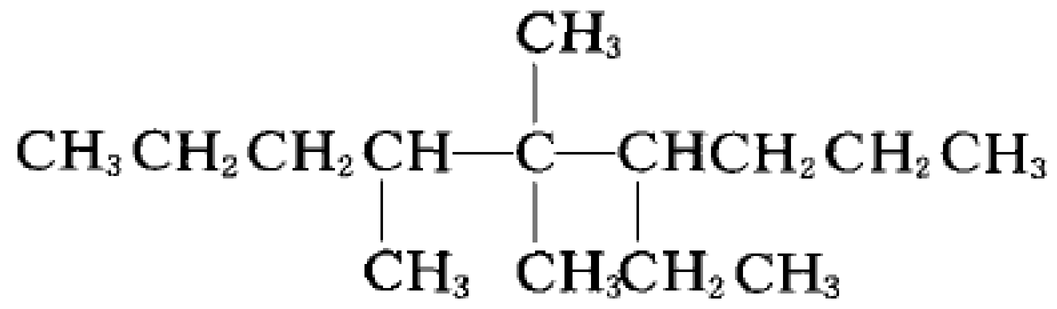


4,4-diisopropylheptane or
4,4-bis (1-methylethyl) heptane

Names such as "isopropyl," "*sec*-butyl," and "*tert*-butyl" are acceptable substituent names in the IUPAC system of nomenclature, but systematic substituent names are preferable.

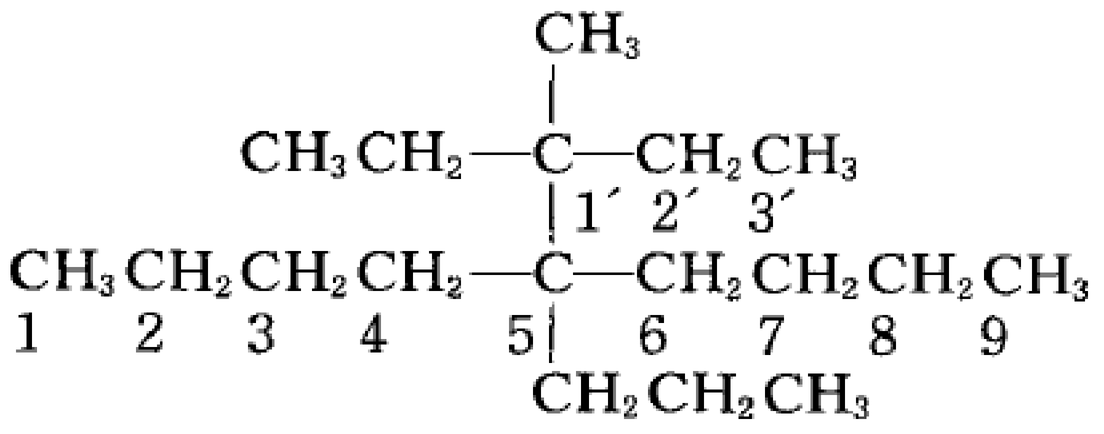
(5)When the full name is constructed, the substituents are listed alphabetically, not numerically. Note that the numbers are separated from one another by a comma and separated from the substituent name by a hyphen. There is no hyphen between the substituent name and the parent name.

The following examples illustrate construction of the name of the branched alkane.



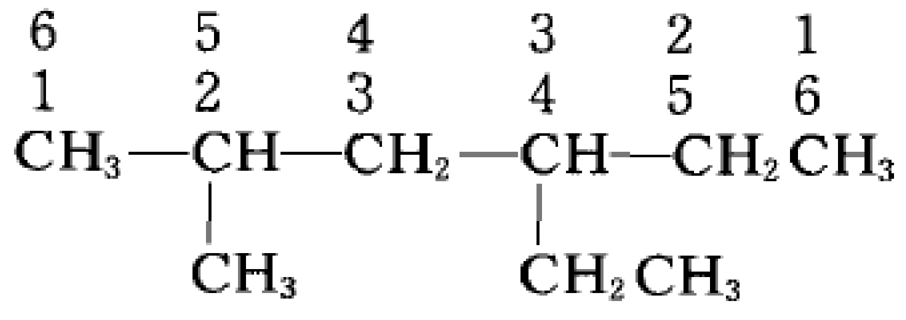
$$CH_3CH_2CH_2\underset{CH_3}{\underset{|}{C}H}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\underset{CH_2CH_3}{\underset{|}{C}H}CH_2CH_2CH_3$$

4-ethyl-5,5,6-trimethylnonane



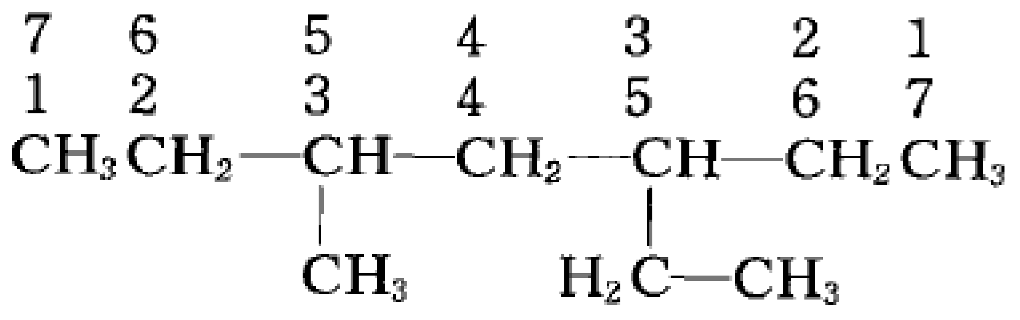
$$CH_3CH_2CH_2CH_2-\overset{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}-CH_2CH_3}{\overset{|}{\underset{CH_2CH_2CH_3}{\underset{|}{C}}}}-CH_2CH_2CH_2CH_3$$

5-(1-ethyl-1-methylpropyl)-5-propylnonane



$$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{CH_2CH_3}{\underset{|}{C}H}-CH_2CH_3$$

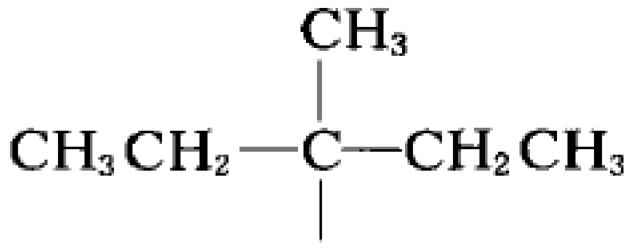
4-ethyl-2-methylhexane (not 3-ethyl-5-methylhexane; the locant set 2,4,is lower than 3,5)



$$CH_3CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2-\underset{H_2C-CH_3}{\underset{|}{C}H}-CH_2CH_3$$

3-ethyl-5-methylheptane (not 5-ethyl-3-methylheptane; *the lower locant must be assigned to the substituent group that is cited first*)

Complex alkyl groups are named by a systematic method using the longest alkyl chain as the base alkyl group. The base alkyl group is numbered beginning with the carbon atom bonded to the main chain. For example, the



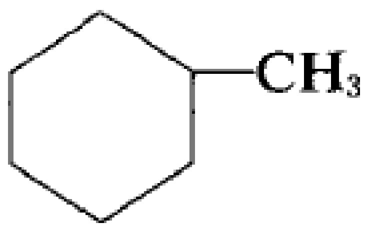
$$CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{C}}-CH_2CH_3$$

group is 1-ethyl-1-methylpropyl.

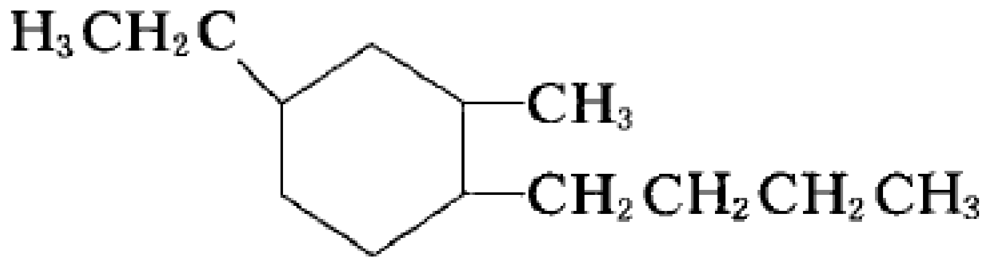
4.2 Naming Cyclic Alkanes

Cycloalkanes are compounds in which the carbon atoms are connected forming one or more rings. Cycloalkanes are named by adding the prefix "**cyclo**" to the alkane name that signifies the number of carbon atoms in the ring. The rules for naming cycloalkanes are essentially the same as those for *acyclic* compounds. There is no need to number the position of a single substituent on a ring. If there is more than one substituent, the substituents are numbered so that they have the lowest possible numbers. Substituents are named alphabetically. If the substituent contains more carbon atoms than those on the ring, the substituent is the parent hydrocarbon and the ring is named as a substituent.

The following examples illustrate construction of the name of the **cyclic alkane**.

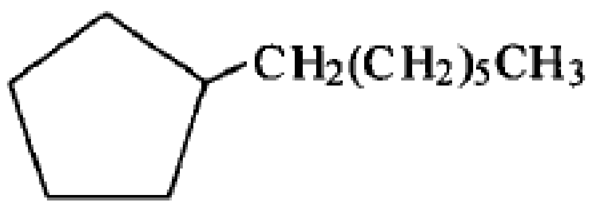


methylcyclohexane



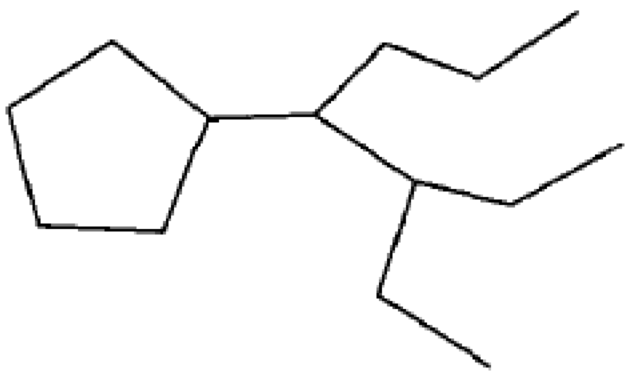
1-butyl-4-ethyl-2-methylcyclohexane

(not 4-butyl-1-ethyl-3-methylcyclohexane, the locant set 1,2,4 is lower than 1,3,4; not 2-butyl-5-ethyl-1-methylcyclohexane, the locant set 1,2,4 is lower than 1,2,5)

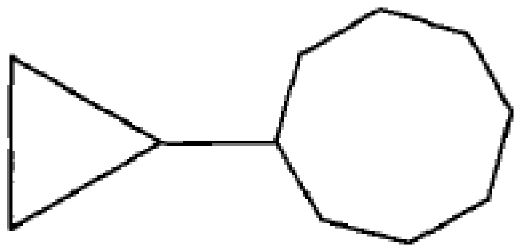


1-cyclopentylheptane

Two or more rings can be joined into *bicyclic* or *polycyclic* systems. The non-detachable prefixes **bicyclo-**, **tricyclo-**, etc. and **spiro**- characterise the



4-cyclopentyl-3-ethylheptane



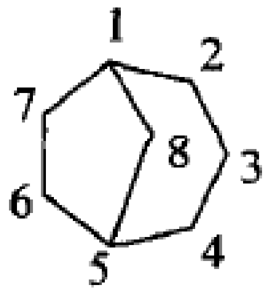
cycloproplycyclooctane

bridged and the spiro systems. Numbers in square brackets give necessary information about the lengths and the positions of the bridges in these polycyclic systems.

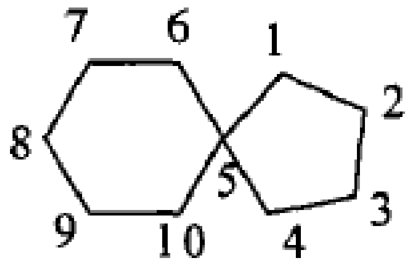
Spirocyclic compounds, in which the two rings share only one carbon atom, are named by placing "**spiro**" before the name of the acyclic parent alkane with the same total number of skeletal atoms. The numbers of skeletal atoms linked to the *spiro* atom in each ring are indicated by Arabic numbers separated by a full stop, cited in ascending order, and enclosed in square brackets; this descriptor is placed between the spiro prefix and the name of the parent hydride. Numbering starts with a ring atom next to the spiro atom and proceeds first through the smaller ring, and then through the spiro atom and around the second ring.

Fused rings share two adjacent carbon atoms and the bond between them. Bridged rings share two nonadjacent carbon atoms (the bridgehead carbons) and one or more carbon atoms (the bridge) between them. All fused and bridged **bicyclic** systems have three bridges connecting the two bridgehead atoms where the rings connect. The name of a bicyclic compound, which follows the prefix **bicyclo** and a set of brackets enclosing three numbers, is based on the name of the alkane having the same number of carbons as there are in the ring system. The system is numbered starting with one of the bridgeheads and proceeding through the longest bridge to the second bridgehead, continuing back to the first bridgehead by means of the longer unnumbered bridge; these two bridges constitute the main ring of the system. The numbers in the brackets give the number of carbon atoms in each of the three bridges connecting the bridgehead carbons, in order of decreasing size.

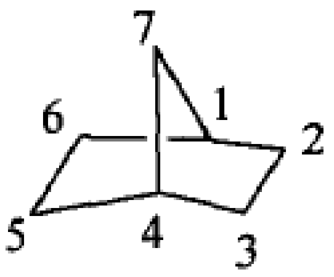
The following examples are named, respectively.



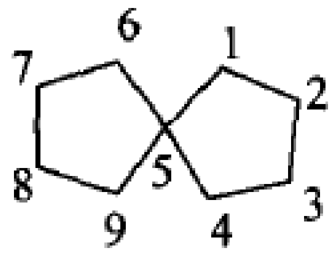
bicyclo[3.2.1]octane



spiro[4.5]decane



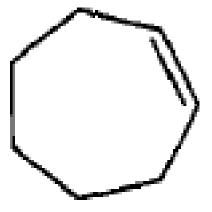
bicyclo[2.2.1]heptane



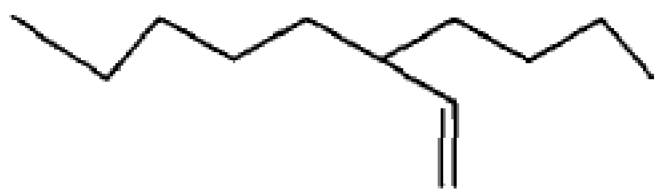
spiro[4.4]nonane

4.3 Nomenclature of Alkenes

Alkenes are hydrocarbons that contain carbon—carbon double bonds. The double bond is the functional group of the alkene. Simple alkenes are named much like alkanes, using the root name of the longest chain containing the double bond, with the **-ane** suffix of an alkane being replaced by **-ene**. For example, "propane" becomes "propene", and "cyclohexane" becomes "cyclohexene". When there is more than one possible location for the double bond in a molecule, a number is used to give the location of the double bond. The longest straight chain (parent alkene) is numbered starting from the end closest to the double bond, and the double bond is given the lower numbers of its two double-bonded carbon atoms. In **cycloalkenes**, the double bond is assigned position number 1.



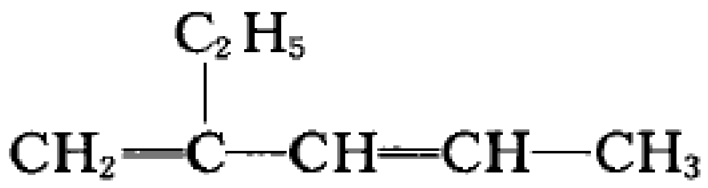
cycloheptene



3-butyl-1-octene

or: 3-butyloct-1-ene

If there is more than one double bond in a compound, the location of each is designated using the same principles. A compound with two double bonds is a **diene**. A **triene** has three double bonds, and a **tetraene** has four. The number of double bonds is indicated by inserting **di-**, **tri-**, before the **-ene** suffixis added to the alkane stem name (Notes: An "**a**" is added if inclusion of **di**, **tri**, etc., would put two consonants consecutively: "buta-1,3-diene", not "but-1,3-diene"). The chain is numbered in the direction that gives the double bonds the lowest possible numbers. The numbers indicating the locations of the double bonds are cited either before the root name or before the suffix. Each alkyl group attached to the main chain is listed with a number to give its location in alphabetical order.

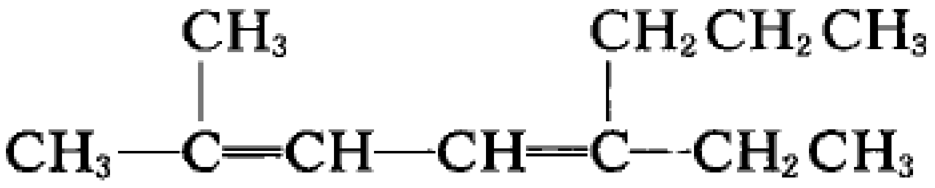


$$CH_2{=}\overset{C_2H_5}{\overset{|}{C}}{-}CH{=}CH{-}CH_3$$

2-ethyl-1,3-pentadiene

or

2-ethylpenta-1,3-diene

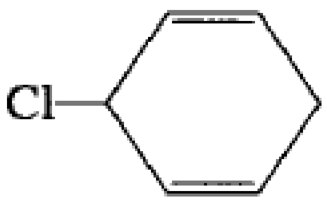


$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH{=}\overset{CH_2CH_2CH_3}{\overset{|}{C}}{-}CH_2CH_3$$

5-ethyl-2-methyl-2,4-octadiene

or

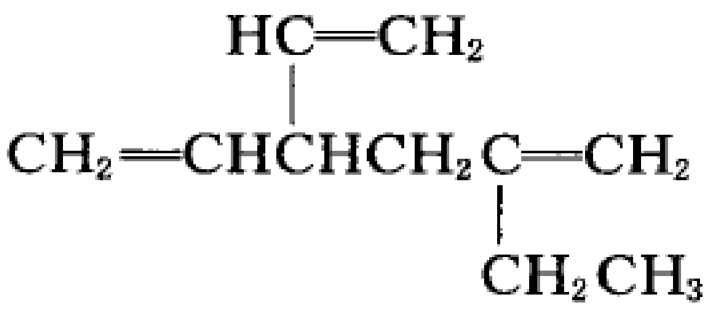
5-ethyl-2-methylocta-2,4-diene



3-chloro-1,4-cyclohexadiene

or

3-chlorocyclohexa-1,4-diene



$$CH_2{=}CH\overset{HC=CH_2}{\overset{|}{C}}HCH_2\underset{\underset{CH_2CH_3}{|}}{C}{=}CH_2$$

2-ethyl-3-vinyl-1,5-hexadiene

or

2-ethyl-3-vinylhexa-1,5-diene

$CH_3CH{=}CHCH{=}CHCH{=}CHCH_3$

2,4,6-octatriene

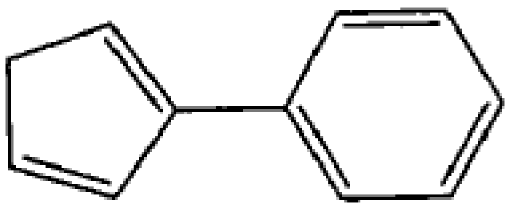
or

octa-2,4,6-triene

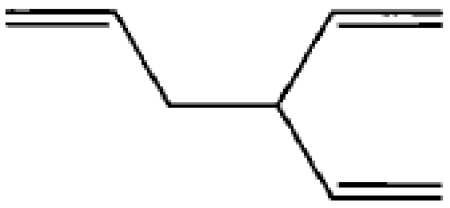
1,3,5,7-cyclooctatetraene

or

cycloocta-1,3,5,7-tetraene



2-phenylcyclopenta-1,3-diene



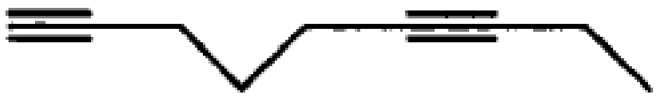
3-vinylhexa-1,5-diene

Most alkenes are conveniently named by the IUPAC system, but common names are sometimes used for the simplest compounds. For example, **ethylene** for ethene, **propylene** for propene, **isobutylene** for 2-methylpropene, the **vinyl** group for ethenyl group, the **allyl** group for 2-propenyl group, and the **methylene** group for methylidene group.

4.4 Nomenclature of Alkynes

Alkynes are named following the IUPAC protocols: choose the longest chain containing the *triple* bond(s) and replace the suffix **-ane** with the suffix **-yne**. Number the carbon atoms from the end of the chain closest to the triple bond and give the lowest number to the first carbon atom in a triple bond. Other substituents on the chain are located using the same numbering sequence with the lowest parent chain numbers possible. A compound with two or more alkyne groups is named using the same numbering principles and the prefixes **di-**, **tri-**. Substituents are given numbers to indicate their locations and listed in alphabetical order.


3-heptyne
or
hept-3-yne


1,6-nonadiyne
or
nona-1,6-diyne

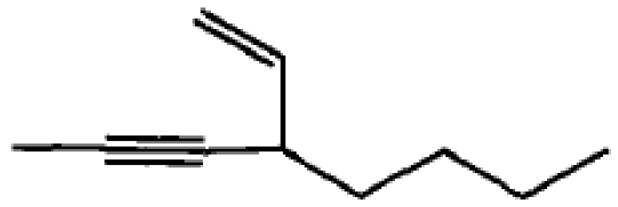
1-chloro-3-hexyne
or
1-chlorohex-3-yne

If both a double bond and a triple bond are present, the chain is numbered in the direction that yields the lowest number in the name of the compound. If the double bond and the triple bond will have the same numbers from either end of the chain, the IUPAC rules give **alkenes** higher priority than **alkynes**, so the numbering of the double bond takes locational priority; that is, the chain is numbered in the direction that gives the double bond the lower number.

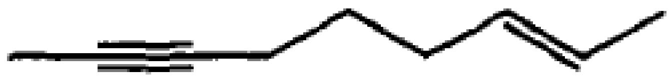
The group obtained by removing a hydrogen from ethyne is called the **ethynyl** group. It can be named as a substituent on a carbon skeleton, as in *ethynyl-cyclohexane*.

In common nomenclature, alkynes are named as **substituted acetylenes**. Most alkynes can be named as a molecule of **acetylene** with one or two alkyl substituents, such as methylacetylene ($CH_3C\equiv CH$), dimethylacetylene ($CH_3C\equiv CCH_3$), ethylmethylacetylene($CH_3C\equiv CCH_2CH_3$). Even the common name alphabetizes the substituents (ethyl before methyl).

2-bromo-6-methyl-3-octyne
or
2-bromo-6-methyloct-3-yne

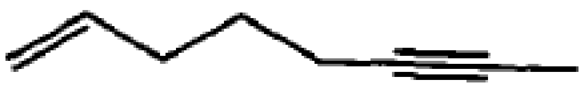


3-butyl-1-hexen-4-yne
or
3-butylhex-1-en-4-yne

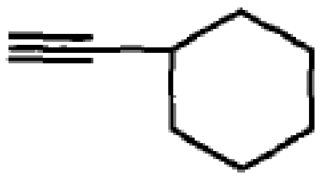


2-nonen-7-yne
or
non-2-en-7-yne

6-octen-1-yne
or
oct-6-en-1-yne



1-octen-6-yne
or
oct-1-en-6-yne

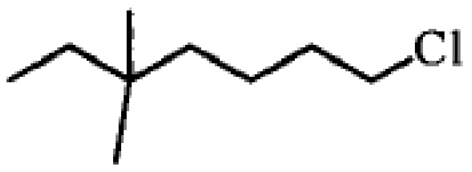


ethynylcyclohexane

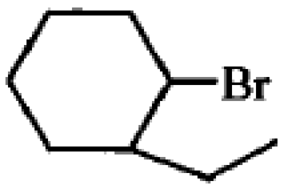
4.5 Nomenclature of Alkyl Halides

Alkyl halides are compounds in which a hydrogen of an alkane has been replaced by a halogen atom: **fluorine**, **chlorine**, **bromine**, or **iodine**. There are two ways of naming alkyl halides. The systematic (IUPAC) nomenclature treats an alkyl halide as an alkane with a **halo-** substituent and listed in alphabetical order with other substituents. The position of each halogen is indicated by a number. The substituent prefix names for the halogens end with "**o**" (i.e. "**fluoro**", "**chloro**", "**bromo**", "**iodo**"). Therefore, alkyl halides are often called **haloalkanes**. The result is a systematic haloalkane name, as in 1-chlorobutane or 2-bromopropane. The common or "trivial" names of many simple haloalkanes consist of the name of the alkyl group, followed by the name of the halogen—with the "**ine**" ending of the halogen name replaced by "**ide**" (i.e. **fluoride**, **chloride**, **bromide**, **iodide**), as in "**cyclopropyl chloride**". This is the origin of the term alkyl halide.

Here are some examples of haloalkanes:

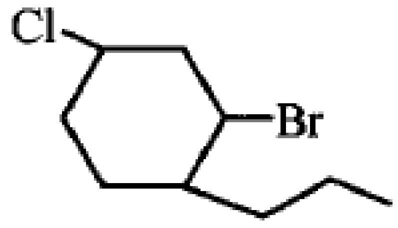


1-chloro-5,5-dimethylheptane

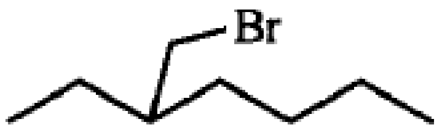


1-bromo-2-ethylcyclohexane

4-(2-fluoroethyl) heptane



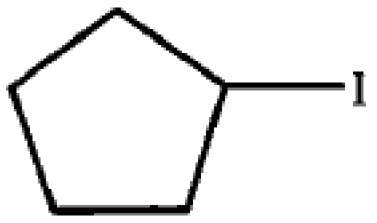
2-bromo-4-chloro-1-propylcyclohexane



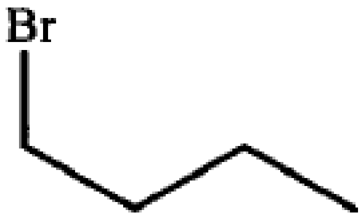
3-(bromomethyl) heptane

1,4-dibromopentane

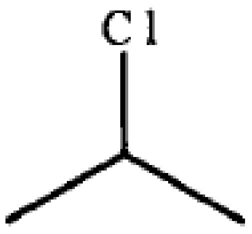
Common names are accepted and used for smaller molecules. Typical common names for alkyl halides are *methyl chloride* (CH_3Cl), *methylene chloride* (CH_2Cl_2), *chloroform* ($CHCl_3$), and *carbon tetrachloride* (CCl_4). The corresponding formal names are *chloromethane*, *dichloromethane*, *trichloromethane* and *tetrachloromethane*. There are analogous common names for other haloalkanes, in which the name of the other halogen replaces chlorine (for example, *bromoform* for $CHBr_3$).



IUPAC: iodocyclopentane
common: cyclopentyl iodide



1-bromobutane
n-butyl bromide



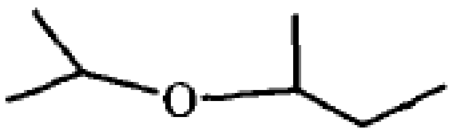
2-chloropropane
isopropyl chloride

4.6 Nomenclature of Ethers

Ethers (ROR′) can be considered derivatives of water (HOH) or alcohols (ROH) in which an oxygen is bonded to two substituents. The substituents in ethers can be alkyl, aryl, or alkenyl, they may be different (an unsymmetrical ether, such as ethyl methyl ether) or the same (a symmetrical ether, such as ethyl ether).

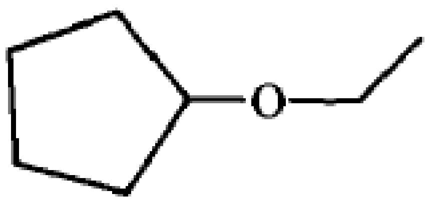
The common name (**Alkyl Alkyl Ether** Names) of an ether consists of the names of the two alkyl substituents (in alphabetical order), followed by the word "**ether**". In a common name for symmetrical ether, the expected *di*-prefix is often not used. For example, *diethyl ether* is often called *ethyl ether*. One group is named in *isopropyl ether*, there must be two isopropyl groups to make the compound an ether.

IUPAC names (**Alkoxy Alkane Names**) use the more complex alkyl group as the root name, and the rest of the ether as an **RO** substituent. The substituents are named by replacing the "**yl**" ending in the name of the alkyl substituent with "**oxy**". The formal name for $CH_3CH_2OCH_2CH_3$ is **ethoxyethane** and the common name is *diethyl ether* (*ethyl ether*).

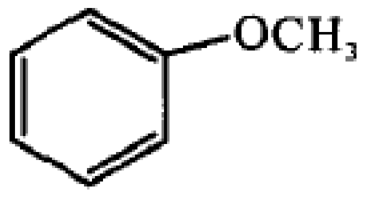


IUPAC: 2-isopropoxybutane
common: *s*-butyl isopropyl ether

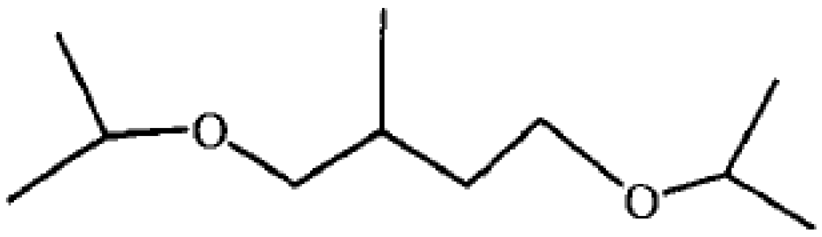
chloromethoxyethane
chloromethyl ethyl ether



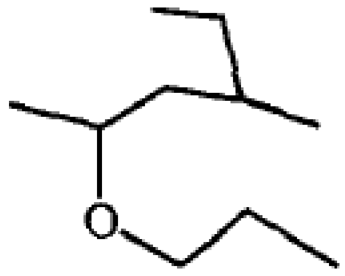
IUPAC: ethoxycyclopentane
common: ethyl cyclopentyl ether



methoxybenzene
methyl phenyl ether

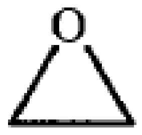


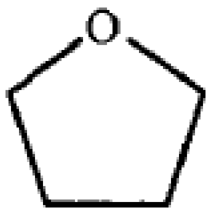
1,4-diisopropoxy-2-methylbutane

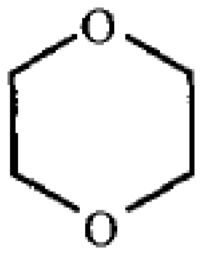


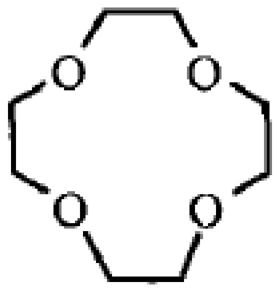
2-propoxy-4-methylhexane

Cyclic ethers are compounds that fit the general ether definition, having a C-O-C linkage, but with that linkage incorporated in a ring. Rings that contain an atom other than carbon are called **heterocyclic compounds**. Cyclic ethers are heterocyclic compounds. The most useful and common cyclic ethers are those with a three-membered ring, known as **epoxides**. The formal name for a saturated five-membered cyclic ether is **oxolane**. The common name for this material is **tetrahydrofuran** (**THF**). A larger cyclic ethers, best known by their historical names **dioxane**, is especially effective reaction solvents. A special class of cyclic ethers containing 10 to 20 atoms, including several oxygen atoms, is called **crown ethers**. Crown ethers are named **[X]-crown-Y**, where **X** is the total number of atoms in the ring and **Y** is the number of oxygen atoms in the ring.



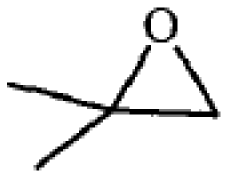




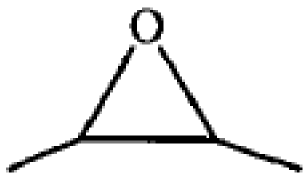


IUPAC:	oxirane	oxolane		
common:	ethylene oxide	tetrahydrofuran	Dioxane	12-crown-4 ether

Cyclic ethers have formal and common names. The IUPAC names for individual saturated three-membered cyclic ethers are based on the name of the unsubstituted parent compound, **oxirane**. Substituents are located on the ring by numbering, starting with the oxygen atom. Another systematic naming method is to name the rest of the molecule and use the term "**epoxy**" as a substituent, giving the numbers of the two carbon atoms bonded to the epoxide oxygen. The common name for a three-membered cyclic ether is derived from the name of the alkene from which it is most commonly prepared, followed by the word "**oxide**", for an alkene oxide.

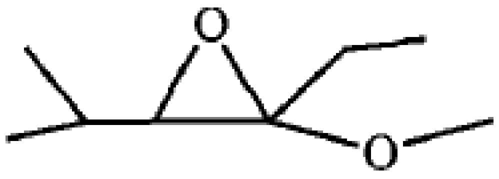


IUPAC: 2,2-dimethyloxirane
2-methyl-1,2-epoxypropane
common: 1,1-dimethylethylene oxide

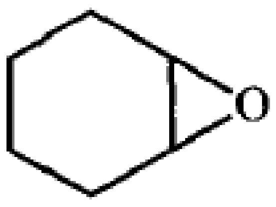


2,3-dimethyloxirane
2,3-epoxybutane
2-butene oxide

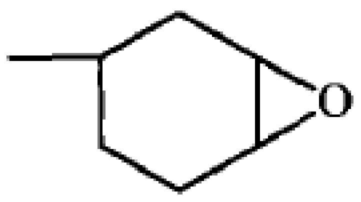
2,3-epoxy-4-methoxyheptane



2-ethyl-3-isopropyl-2-methoxyoxirane



cyclohexene oxide

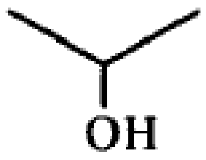
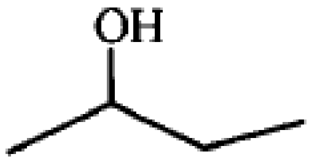


1,2-epoxy-4-methylcyclohexane

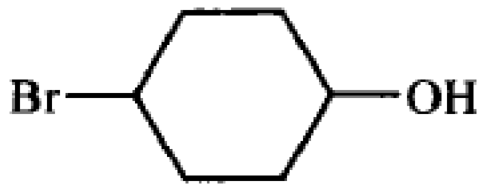
4.7 Nomenclature of Alcohols

Alcohols are classified as **primary**, **secondary**, or **tertiary**, depending on whether the **—OH** group is bonded to a primary, secondary, or tertiary carbon. The common name of an alcohol consists of the name of the alkyl group to which the —OH group is attached, followed by the word "**alcohol**": **alkyl alcohol**. If the structure is complex, the common nomenclature becomes awkward, and the IUPAC nomenclature should be used.

The following rules are used to name an alcohol. Name the longest continuous chain containing the —OH group. Drop the final **-e** from the parent hydrocarbon name and add the suffix **-ol** to give the root name. If there is a hydroxyl group and a substituent, number the longest carbon chain in the direction that gives the hydroxyl group suffix the lowest possible number. (The hydroxyl group takes precedence over double and triple bonds.). If there is more than one substituent, name all the substituents and give their numbers, the substituents are cited in alphabetical order. If the same number for the hydroxyl group is obtained in both directions, the chain is numbered in the direction that gives substituents lower possible number.

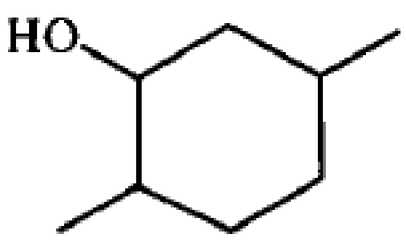
				
IUPAC:	propan-1-ol	propan-2-ol	prop-2-en-1-ol	butan-2-ol
common:	*n*-propyl alcohol	isopropyl alcohol	allyl alcohol	*sec*-butyl alcohol

Cyclic alcohols are named using the prefix "**cyclo-**"; the hydroxyl group is assumed to be on C 1 .



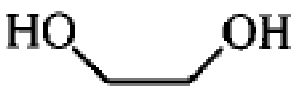
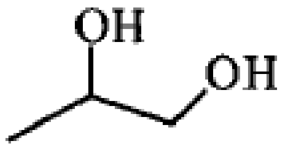
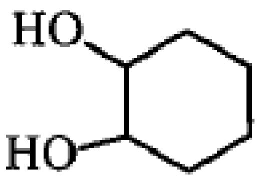
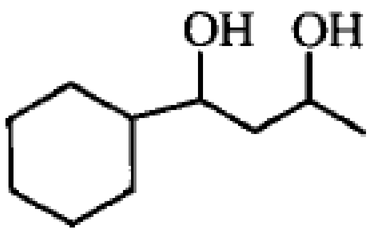
4-bromocyclohexan-1-ol

1-ethylcyclopentan-1-ol



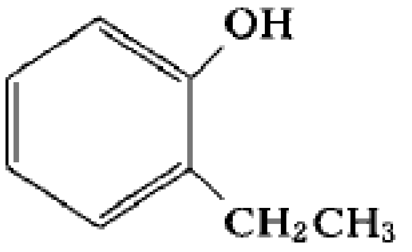
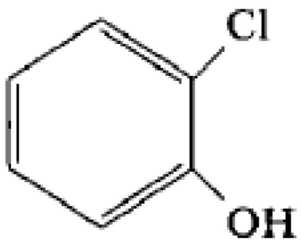
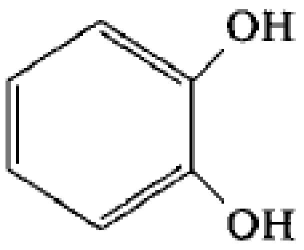
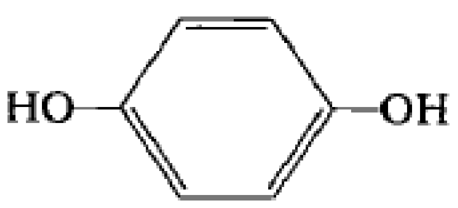
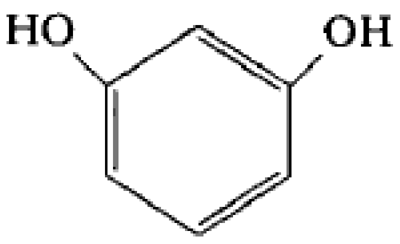
2,5-dimethylcyclohexan-1-ol

If more than one hydroxyl group is present, the name becomes **-diol**, **-triol**, etc., with numbers needed to tell where the hydroxyl groups are located. The terminal **-e** in the parent name is not dropped. For example, ethane with two hydroxyl groups would become **ethane + diol**, not *ethan + diol*.

				
IUPAC:	ethane-1,2-diol	propane-1,2-diol	cyclohexane-1,2-diol	1-cyclohexylbutane-1,3-diol
common:	ethylene glycol	propylene glycol	cyclohexane glycol	

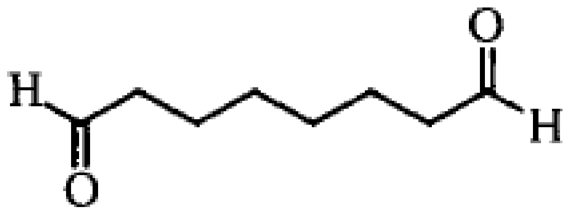
The common name "**glycol**" generally means a **vicinal diol**, with its two hydroxyl groups on adjacent carbon atoms.

Although **phenol** is an alcohol, its properties are quite different from "normal" alcohols. Phenol and similar ring compounds are called aromatic or aryl alcohols. The following examples illustrate the systematic names and the common names of some phenolic compounds.

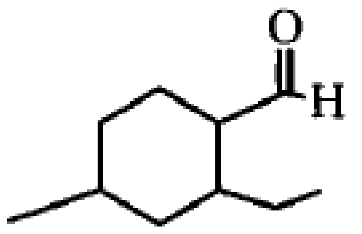
					
IUPAC:	2-ethylphenol	2-chlorophenol	benzene-1,2-diol	benzene-1,4-diol	benzene-1,3-diol
common:	*o*-ethylphenol	*o*-chlorophenol	catechol	hydroquinone	resorcinol

4.8 Nomenclature of Aldehydes

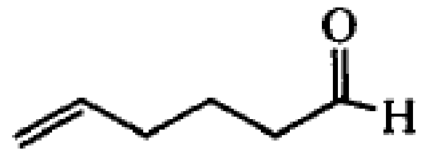
The **aldehyde** group is symbolized by **-CHO**, implying that the hydrogen is attached to the carbonyl carbon. The nomenclature of aldehydes follows the same general rules given for alkanes. The longest carbon-carbon chain containing the aldehyde group is chosen as the parent. The carbonyl carbon atom in aldehydes is at the end of a chain, so it is numbered 1. The parent chain name is based on that of the corresponding alkane, alkene, or alkyne where the terminal -e is replaced by **-al**. Other substituents, including hydroxyl, amino, and alkoxy groups and multiple carbon-carbon bonds, are designated by numerical positions relative to the aldehyde. If the aldehyde group is attached to a ring, the aldehyde is named by adding "**carbaldehyde**" to the name of the cyclic compound (for example, *cyclohexanecarbaldehyde*). If there is an aldehyde at each end of the parent chain, the molecule is a **-dial** and the terminal **-e** in the alkane name is not dropped when naming **di-** or **polyaldehydes.** If the compound has both an alkene and an aldehyde functional group, the alkene is cited first, with the "e" ending omitted to avoid two successive vowels. In the case of *benzenoid aldehydes*, the parent IUPAC name *benzenecarbaldehyde* is almost never used. Instead, the common name **benzaldehyde** is used, and substituents are designated by name and position.



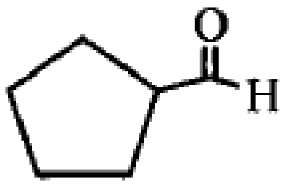
octanedial



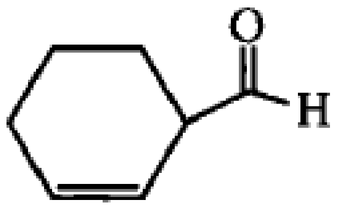
2-ethyl-4-methylcyclohexanecarbaldehyde



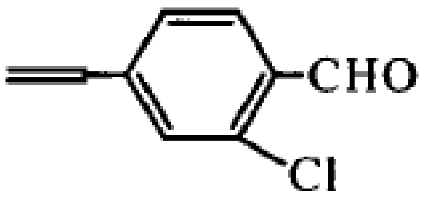
5-hexenal



cyclopentanecarbaldehyde

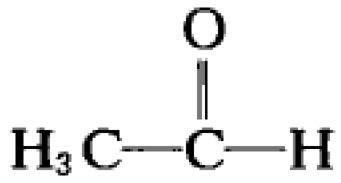


2-cyclohexenecarbldehyde

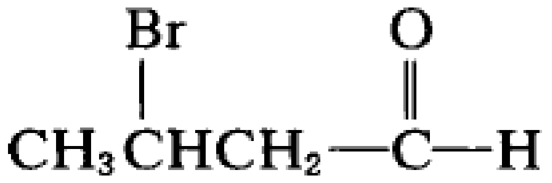


2-chloro-4-vinylbenzaldehyde

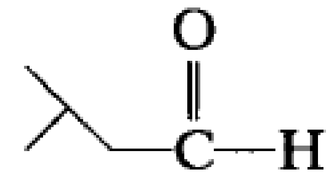
The common name of an aldehyde is the same as the common name of the corresponding carboxylic acid, except that "aldehyde" is substituted for "**ic acid**" (or "**oic acid**"). **Formaldehyde** (HCHO) is named after formic acid. **Acetaldehyde** (CH_3CHO) is named after acetic acid. **Benzaldehyde** (C_6H_5CHO) is named after benzoic acid. When common names are used, the position of a substituent is designated by a lower case Greek letter. The carbonyl carbon is not designated; the carbon adjacent to the carbonyl carbon is called the **alpha** (**α**) carbon atom(s). The next carbon atom is called the **beta** (**β**) carbon atom. The third is called the **gamma** (**γ**) carbon atom, etc.



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H$



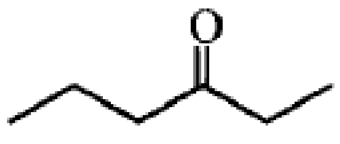
$CH_3\overset{\overset{\displaystyle Br}{|}}{C}HCH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

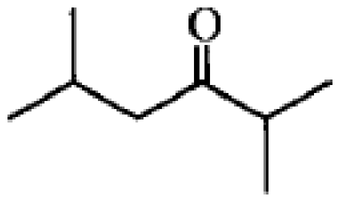


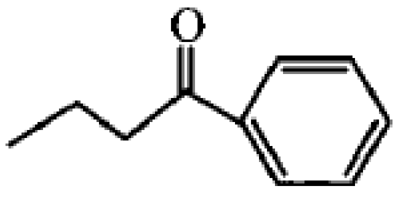
IUPAC:	ethanal	3-bromobutanal	3-methylbutanal
common:	acetaldehyde	β-bromobutyraldehyde	isovaleraldehyde

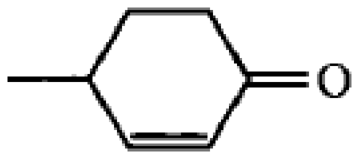
4.9 Nomenclature of Ketones

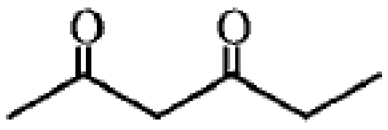
Systematic names of **ketones** are derived by replacing the terminal **-e** in the corresponding alkane, alkene, or alkyne name with **-one**. The "**alkane**" name becomes "**alkanone**". In linear ketones having more than four carbon atoms, the longest chain that includes the carbonyl carbon was numbered from the end closest to the carbonyl group, the carbonyl carbon was given the smaller number. The position of the carbonyl group was indicated by a number. In cyclic ketones, the carbonyl carbon atom of a cyclic ketone is alway assigned the number 1. Molecules with more than one ketone group (polyketones) are called **-diones**, **-triones**, etc. The terminal **-e** of the alkane is not dropped in naming polyketones (for example, 2,4-pentanedione or pentane-2,4-dione).

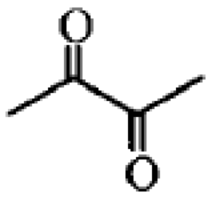

3-hexanone
hexan-3-one


2,5-dimethyl-3-hexanone
2,5-dimethylhexan-3-one

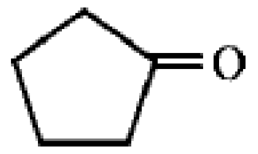

1-phenyl-1-butanone
1-phenylbutan-1-one


4-methyl-2-cyclohexenone
4-methylcyclohex-2-en-1-one


2,4-hexanedione


butanedione

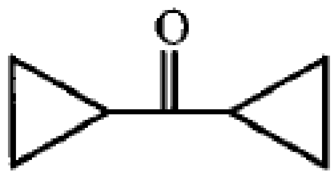

6-hepten-2-one


cyclopentanone

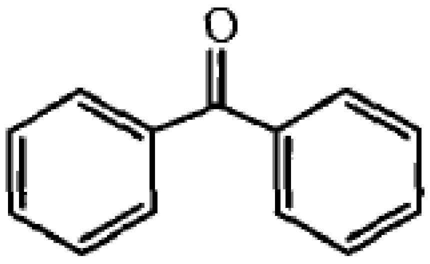
Common names are often used for lower-molecular-weight ketones, including *acetone*, *acetophenone* and *benzophenone*. Many ketones are referred to by the names of the two substituents attached to the carbonyl group followed by "**ketone**". When the two substituent groups in the ketone are not identical, they are cited in alphabetical order. For example, $CH_3COCH_2CH_3$ is *ethyl methyl ketone*. If the two groups are identical, ketones are named as dialkyl or diaryl ketones. In common names, the carbon atom(s) bonded directly to the carbonyl carbon atom (on both sides for ketones) is/are called the **alpha** (**α**) carbon atom(s). The next carbon atom is called the **beta** (**β**) carbon atom. The third is called the **gamma** (**γ**) carbon atom, etc., following the order of letters in the Greek alphabet.


acetone

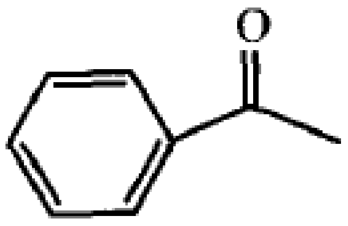

butyl methyl ketone


dicyclopropyl ketone

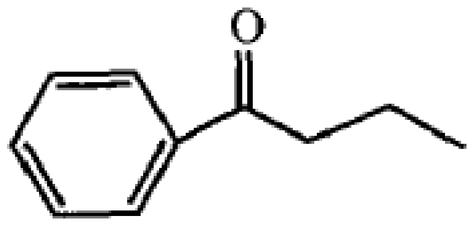
Common names are also used for some *phenyl-substituted* ketones; the number of carbons (other than those of the phenyl group) is indicated by the common name of the corresponding carboxylic acid, substituting "**ophenone**" for "**ic acid**".



benzophenone
diphenyl ketone



acetophenone
methyl phenyl ketone



butyrophenone
phenyl propyl ketone

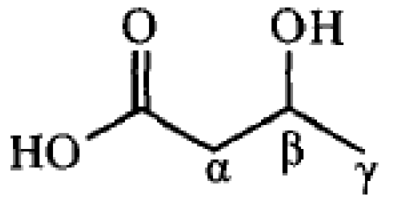
4.10 Nomenclature of Carboxylic Acids

The combination of a *carbonyl* group (—CO—) and a *hydroxyl* group (—OH) on the same carbon atom is called a **carboxyl group** (**—COOH**). Compounds containing the carboxyl group are distinctly acidic and are called **carboxylic acids**.

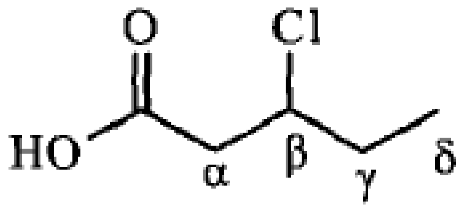
Carboxylic acids are classified according to the substituent bonded to the carboxyl group. An **aliphatic acid** has an alkyl group bonded to the carboxyl group, and an aromatic acid has an aryl group.

Many carboxylic acids have very long histories and were assigned names long before their structures were known or IUPAC nomenclature existed. Several aliphatic carboxylic acids initially isolated from natural sources have been known for hundreds of years, and given their common names (in Latin or Greek) based on their historical sources. **Formic acid** (HCOOH) was extracted from ants (formica, Latin for ants). **Acetic acid** (CH_3COOH) was isolated from vinegar (vinegar, Latin for acetum).

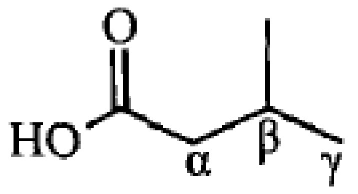
In common names of an aliphatic carboxylic acid, the positions of substituents are preceded by the Greek letters **α**, **β**, **γ**, **δ**, **ε** etc. The position of the carbon atom next to the carboxyl group is called the α-position. The next positions, in order, are called β, γ and δ. Thus, **β-hydroxybutyric acid** is the common name for **3-hydroxybutanoic acid**.



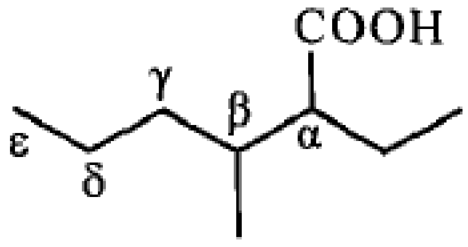
β-hydroxybutyric acid



β-chlorovaleric acid



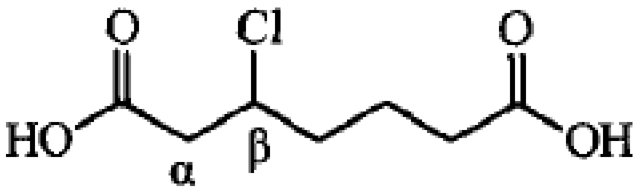
β-methylbutyric acid



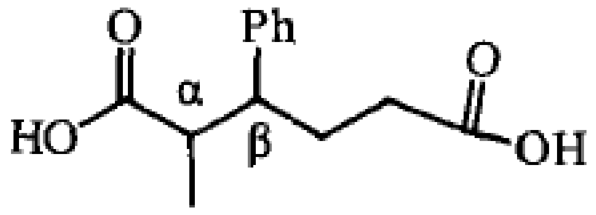
α-ethyl-β-methylcaproic acid

Long chain carboxylic acids are often called **fatty acids**, many of them were first obtained by hydrolysis of fats. *Oleic acid* is an unsaturated fatty acid. *Lauric acid*, *myristic*, *palmitic* and *stearic* acids are the most common saturated fatty acids.

A **dicarboxylic acid** (also called a **diacid**) is a compound with two carboxyl groups. The common names of simple dicarboxylie acids are used more frequently than their systematic names. A common mnemonic for the common names of the first five dicarboxylic acids is "**Oh my, such good apple pie**", standing for *oxalic*, *malonic*, *succinic*, *glutaric*, *adipic* and *pimelic* acids. Substituted dicarboxylic acids are given common names using Greek letters, as with the simple carboxylic acids. Greek letters are assigned beginning with the carbon atom adjacent to the carboxyl group that is closer to the substituents.

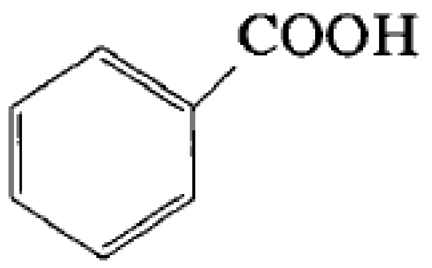


β-chloropimelic acid

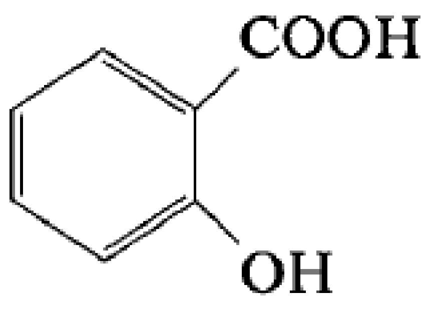


α-methyl-β-phenyladipic acid

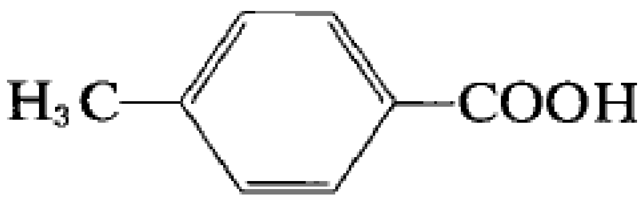
Aromatic carboxylic acids are usually referred to by their historical names. The simplest aromatic carboxylic acid is *benzoic acid*. If benzoic acid contains one substituent, its position can be indicated by the prefix ***ortho-*** (***o-***), ***meta-*** (***m-***), ***or para-*** (***p-***). Benzenoid compounds with two carboxyl groups are named *phthalic acids*. Phthalic acid itself is the *ortho* isomer. The *meta* isomer is called *isophthalic acid*, and the *para* isomer is called *terephthalic acid*. Many aromatic acids have historical names that are unrelated to their structures.



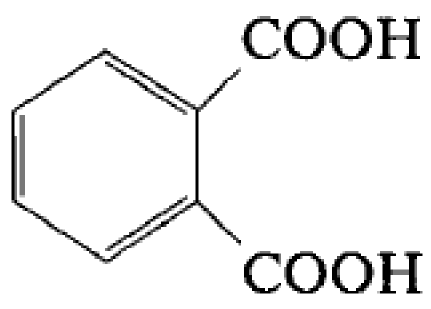
benzoic acid



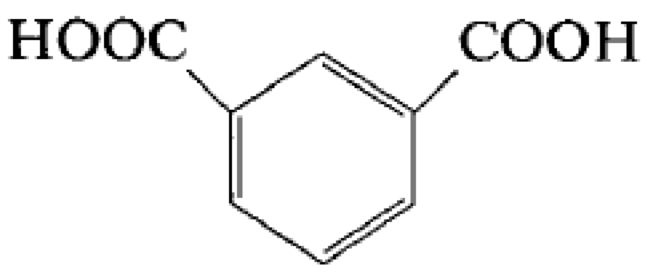
o-hydroxybenzoic acid
(salicylic acid)



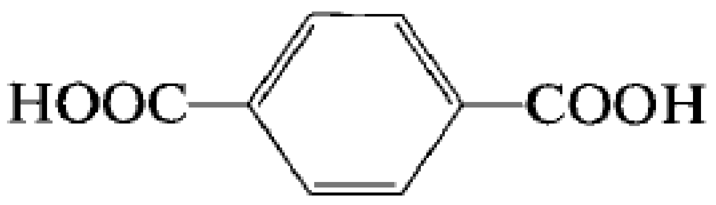
p-methylbenzoic acid
(*p*-toluic acid)



o-phthalic acid
phthalic acid

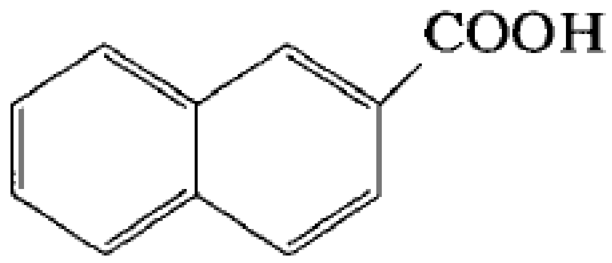


m-phthalic acid
isophthalic acid



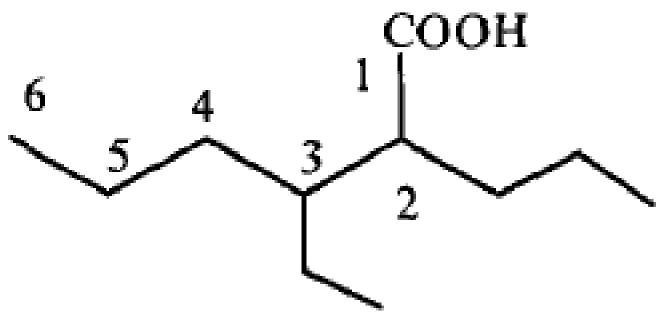
p-phthalic acid
terephthalic acid

Polynuclear aromatic hydrocarbon (PAH) carboxylic acids are named in a similar way, for example, *β-naphthoic acid* (from *naphthalene*).

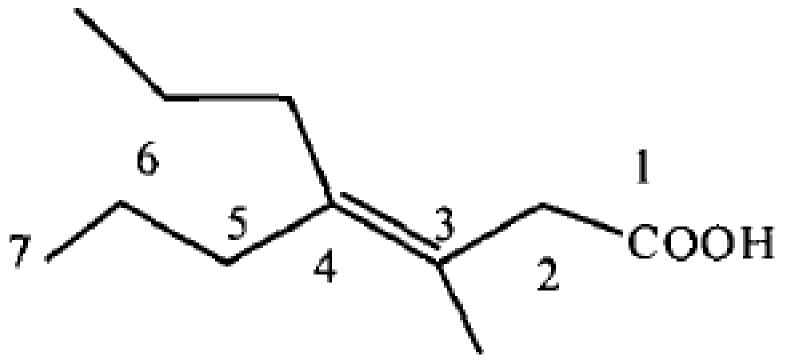


β-naphthoic acid

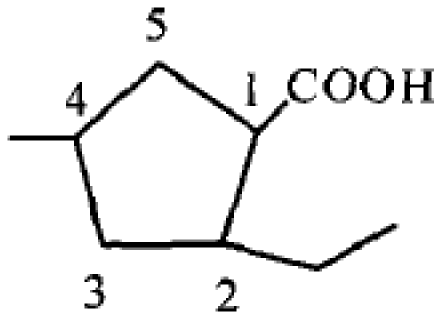
The IUPAC nomenclature for carboxylic acids is based on the longest, continuous chain of carbon atoms containing the carboxyl group as the terminal group. The final **-e** in the name of the corresponding alkane, alkene, or alkyne is replaced by the suffix "**-oic acid**". The chain is numbered, starting with the carboxyl carbon atom, to give positions of substituents along the chain. Substituents (branches) are named alphabetically. The carbon atom in the carboxyl group is always carbon atom number one (C－1). In naming, the carboxyl group takes priority over any of the functional groups discussed previously. Aliphatic rings with carboxyl group (—COOH) substituents are named by adding the words "**carboxylic acid**" to the ring name, as in *cyclobutanecarboxylic acid*. (Note that the terminal **-e** of the alkane name is retained because the next letter in the name is not a vowel.). Ring substituents can be assigned numbers to indicate their position on the ring (the carboxyl group is always on ring carbon atom C－1).



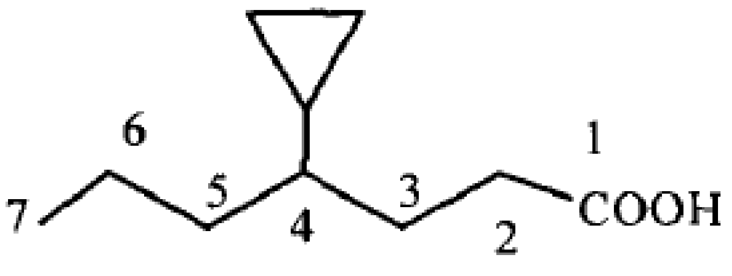
3-ethyl-2-propylhexanoic acid



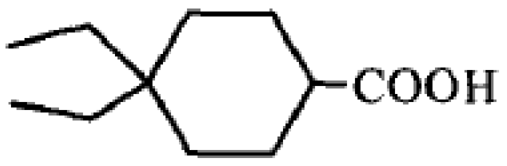
3-methyl-4-propylhept-3-enoic acid



2-ethyl-4-methylcyclopentanecarboxylic acid

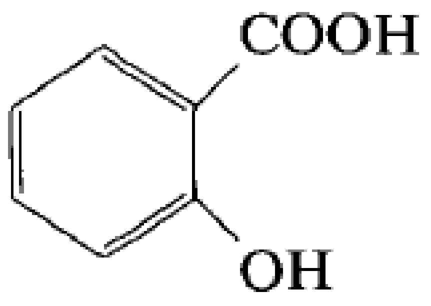


4-cyclopropylheptanoic acid

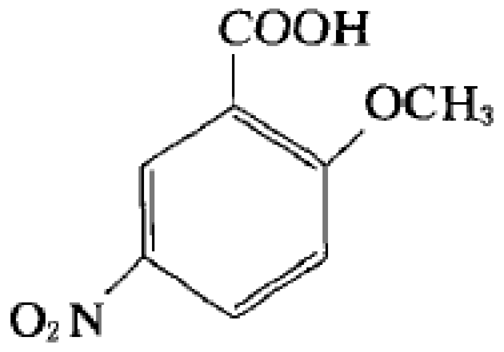


4,4-diethylcyclohexanecarboxylic acid

Aromatic acids of the form Ar—COOH are named as derivatives of *benzenecarboxylic acid* (C_6H_5COOH). However, this name is seldom used; instead, the historical name ***benzoic acid*** is used. As with other aromatic compounds, the numbering system (1, 2, etc.) is used if there are more than one substituent on the aromatic ring.



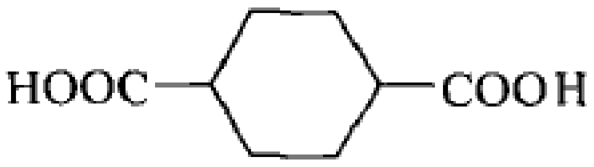
2-hydroxybenzoic acid
(salicylic acid)



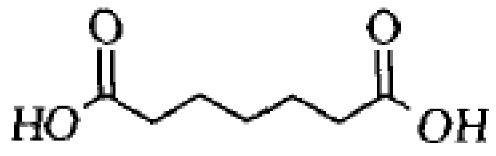
2-methoxy-5-nitrobenzoic acid

Straight chain dicarboxylic acids are named simply by adding the suffix "**-dioic acid**" to the name of the parent name. The parent name is determined by using the longest continuous chain that contains both carboxyl groups. The chain is numbered beginning with the carboxyl carbon atom that is closer to the substituents, and these numbers are used to give the positions of the substituents. The system for naming **cyclic dicarboxylic acids** are based on the name of the parent name, and the suffix **dicarboxylic acid** is added without dropping the terminal **-e** in the parent name. The IUPAC and common names of some carboxylic acids are shown in Table 4.3.

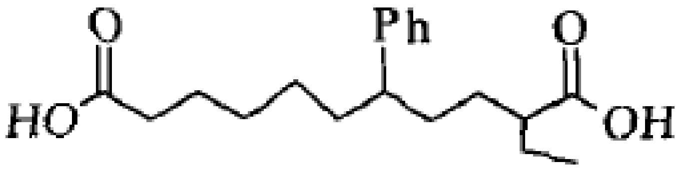
propanedioic acid



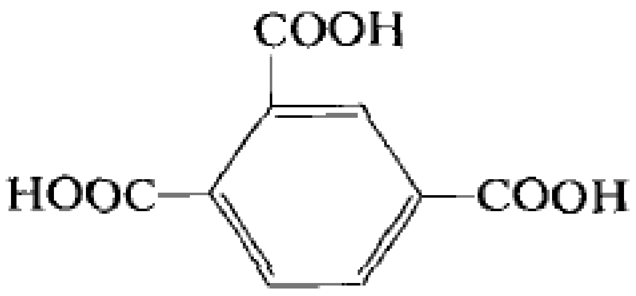
1,4-cyclohexanedicarboxylic acid



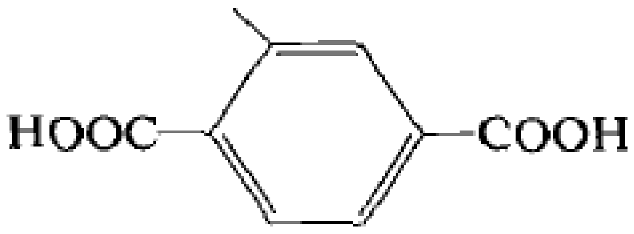
heptanedioic acid



2-ethyl-5-phenylundecanedioic acid

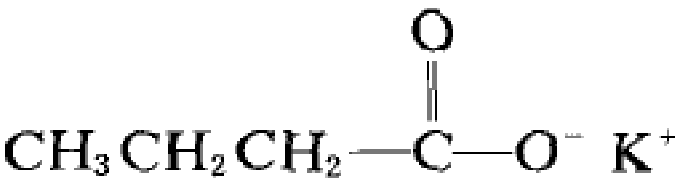


1,2,4-benzenetricarboxylic acid



2-methyl-1,4-benzenedicarboxylic acid

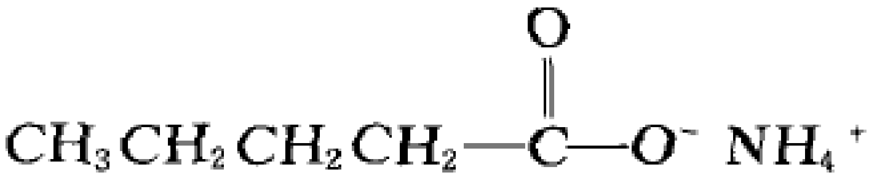
Salts of carboxylic acids are made by replacing the acid hydrogen ($-CO_2H$) with a metal (or ammonium) cation ion. Salts of carboxylic acids are named simply by first naming the cation, then naming the carboxylate ion by replacing the suffix **"-ic acid"** part of the acid name with **"-ate"**. The sodium salt of acetic acid (CH_3CO_2H) is called *sodium acetate* ($CH_3CO_2^-\ Na^+$).



$$CH_3CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O^-\ K^+$$

potassium butanoate

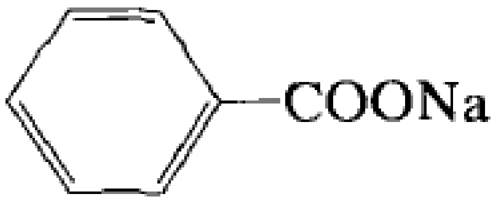
potassium butyrate



$$CH_3CH_2CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-O^-\ NH_4^+$$

ammonium pentanoate

ammonium valerate



sodium benzoate

Table 4.3 IUPAC and common names of some carboxylic acids

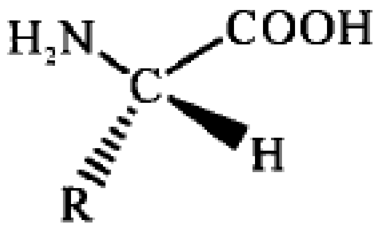
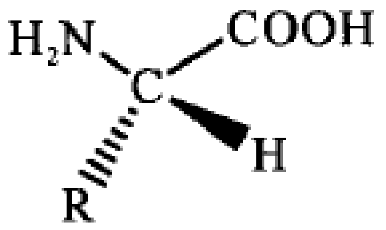
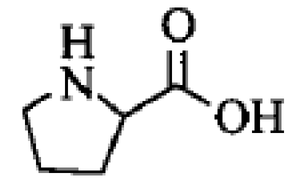
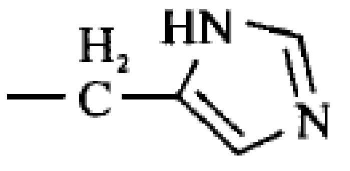
Structure	Common Name (+ acid)	IUPAC Name (+ acid)
$HCOOH$	formic	methanoic
CH_3COOH	acetic	ethanoic
CH_3CH_2COOH	propionic	propanoic
$CH_3(CH_2)_2COOH$	butyric	butanoic
$CH_3(CH_2)_3COOH$	valeric	pentanoic

Continued

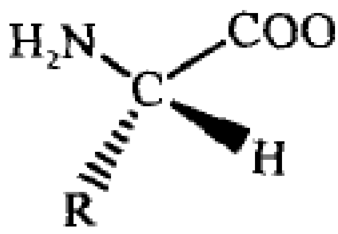
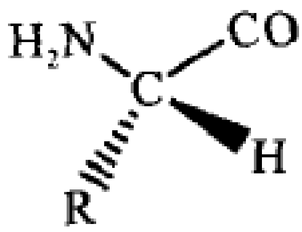
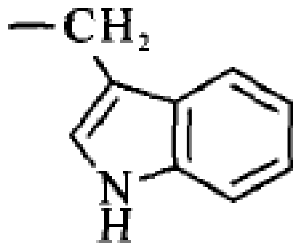
Structure	Common Name (+ acid)	IUPAC Name (+ acid)
$(CH_3)_2CHCH_2COOH$	isovaleric	3-methylbutanoic
$(CH_3)_3CCOOH$	pivalic	2,2-dimethylpropanoic
$CH_3(CH_2)_4COOH$	caproic	hexanoic
$CH_3(CH_2)_6COOH$	caprylic	octanoic
$CH_3(CH_2)_8COOH$	capric	decanoic
$CH_3(CH_2)_{10}COOH$	lauric	dodecanoic
$CH_3(CH_2)_{12}COOH$	myristic	tetradecanoic
$CH_3(CH_2)_{14}COOH$	palmitic	hexadecanoic
$CH_3(CH_2)_{16}COOH$	stearic	octadecanoic
$CH_2{=}CHCOOH$	acrylic	2-propenoic
$CH_3CH{=}CHCOOH$	crotonic	*trans*-2-butenoic
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	oleic	*cis*-9-octadecenoic
$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	linoleic	*cis*, *cis*-9, 12-octadecadienoic
$HOOC{-}COOH$	oxalic	ethanedioic
$HOOCCH_2COOH$	malonic	propanedioic
$HOOC(CH_2)_2COOH$	succinic	butanedioic
$HOOC(CH_2)_3COOH$	glutaric	pentanedioic
$HOOC(CH_2)_4COOH$	adipic	hexanedioic
$HOOCCH{=}CHCOOH$	maleic	*cis*-2-butenedioic
$HOOCCH{=}CHCOOH$	fumaric	*trans*-2-butenedioic
C_6H_5COOH	benzoic	benzoic
$o{-}CH_3C_6H_4COOH$	*o*-toluic	2-methylbenzoic
$1,2\text{-}C_6H_4(COOH)_2$	phthalic	Benzene-1,2-dicarboxylic
$1,3\text{-}C_6H_4(COOH)_2$	isophthalic	Benzene-1,3-dicarboxylic
$1,4\text{-}C_6H_4(COOH)_2$	terephthalic	Benzene-1,4-dicarboxylic

An **amino acid** is an organic compound that possesses both amine (—NH_2) and carboxyl (—COOH) groups within the same organic framework. When both functional groups are attached to the same carbon atom, they are designated **α-amino acids**. These are of special significance in biology as they form the diverse monomer set from which peptides and proteins are built. The twenty biologically most important α-amino acids may be named systematically. For example, when R is methyl, the compound may be called **2-methylaminoacetic acid**. It may also correctly be called **2-aminopropanoic acid**. By far, however, it is most commonly called **alanine**. With the exception of *glycine* (R = H), the natural amino acids are chiral, with the S configuration at the α-carbon. They all are primary amines, except for *proline* which is a 2° amine. The IUPAC uses the three-letter abbreviations shown in the second column of Table 4.4 to describe amino acids. These are widely used in biological circles as well.

Table 4.4 The names and structures of the twenty natural amino acids

Natural α-Amino Acids 		Name	Natural α-Amino Acids 		Name
Symbol	R		Symbol	R	
Gly	—H	Glycine	Glu	—$CH_2CH_2CH_2CO_2H$	Glutamic acid
Ala	—CH_3	Alanine	Gln	—$CH_2CH_2CH_2C(O)NH_2$	Glutamine
Val	—$CH(CH_3)_2$	Valine	Lys	—$CH_2CH_2CH_2CH_2NH_2$	Lysine
Leu	—$CH_2CH(CH_3)_2$	Leucine	Arg	—$CH_2CH_2CH_2NH$—$C(NH)NH_2$	Arginine
Pro		Proline	His		Histidine
Ile	—$CH(CH_3)CH_2CH_3$	Isoleucine	Cys	—CH_2SH	Cysteine

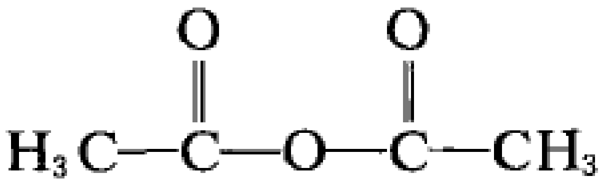
Continued

Natural α-Amino Acids 		Name	Natural α-Amino Acids 		Name
Symbol	R		Symbol	R	
Ser	$-CH_2OH$	Serine	Met	$-CH_2CH_2SH$	Methionine
Thr	$-CH(OH)CH_3$	Threonine	Phe	$-C_6H_5$	Phenylalanine
Asp	$-CH_2CH_2CO_2H$	Aspartic acid	Tyr	$-C_6H_4OH$	Tyrosine
Asn	$-CH_2CH_2CONH_2$	Asparagine	Trp		Tryptophan

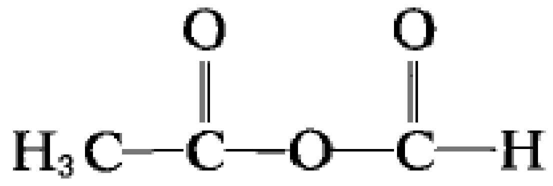
4.11 Nomenclature of Anhydrides

Anhydride means "without water". Two carboxylic acid molecules eliminate a molecule of water, results in an acid anhydride.

Anhydrides are named using the name of the parent carboxylic acid from which it is formed, and replacing the word **"acid"** with **"anhydride"** in both the formal and the common names. If the two carboxylic acid molecules forming the acid anhydride are the same, the anhydride is a symmetrical anhydride. Symmetrical anhydrides are sometimes called **bis anhydrides**, e. g. *bisacetic anhydride*, usually the prefix **"bis"** is eliminated, *acetic anhydride*. If the two carboxylic acid molecules are different, the anhydride is a mixed anhydride. Mixed anhydrides are stating the names of both acids in alphabetical order, for example, *ethanoic methanoic anhydride* is formal name and acetic formic anhydride is the common name.

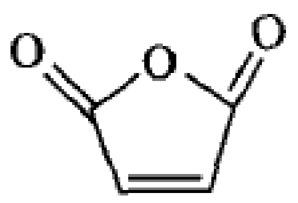


$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$



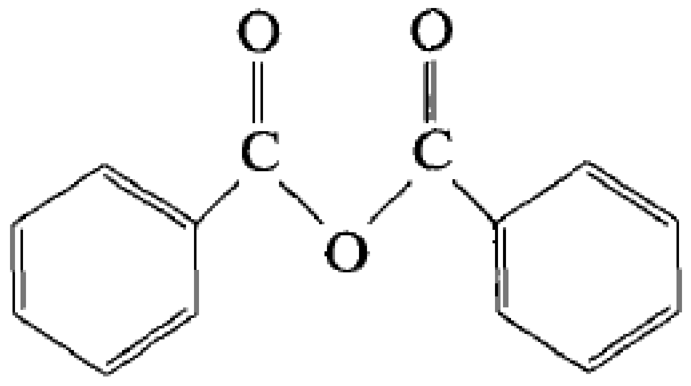
$H_3C-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-H$

common:	acetic anhydride	acetic formic anhydride	succinic anhydride
IUPAC:	ethanoic anhydride	ethanoic methanoic anhydride	butanedioic anhydride

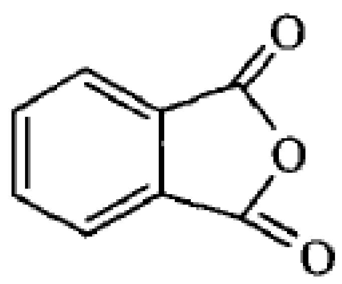


maleic anhydride

2-butenedioic anhydride



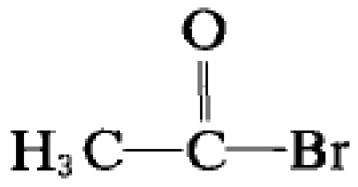
benzoic anhydride



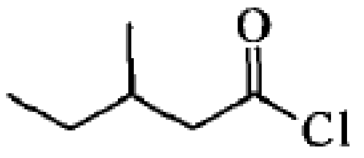
phthalic anhydride

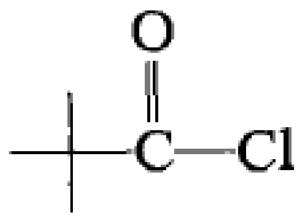
4.12 Nomenclature of Acyl Halides

Carboxylic acid halides are often just called **acid halides** or **acyl halides**. Acyl halides are compounds that have a halide atom attached to a carbonyl group, in place of the —OH group of a carboxylic acid. The most common acyl halides are acyl chlorides and acyl bromides. Acid chlorides are named on the basis of the carboxylic acid from which they are derived. Acyl halides are named by using the acid name and replacing "**ic acid**" with "**yl chloride**" (or "**yl bromide**"). For acids ending with "**carboxylic acid**", "**carboxylic acid**" is replaced with "**carbonyl chloride**" (or "**carbonyl bromide**"). The same rule applies to both IUPAC and common names. For example, *p-toluenesulfonic acid* (TsOH) becomes *p- toluenesulfonyl chloride* (TsCl). Cyclic carboxylic acids become carbonyl halides. *Cyclopentanecarboxylic acid* becomes *cyclopentanecarbonyl chloride*.

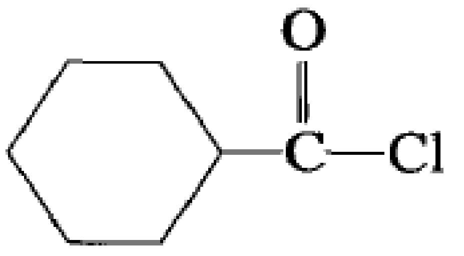


$H_3C-\overset{O}{\overset{\|}{C}}-Br$

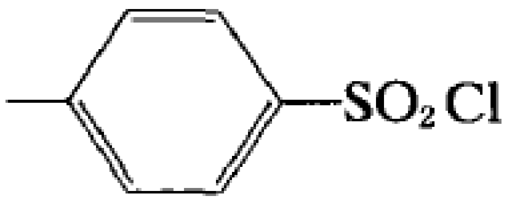




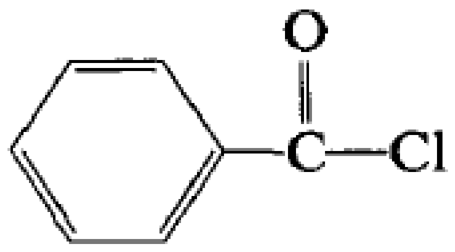
IUPAC:	ethanoyl bromide	3-methylpentanoyl chloride	2,2-dimethylpropanoyl chloride
common:	acetyl bromide	β-methylvaleryl chloride	pivalyl chloride



cyclohexanecarbonyl chloride



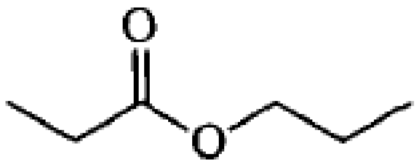
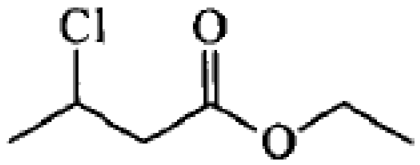
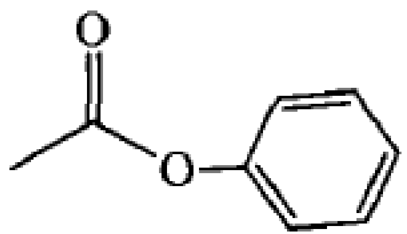
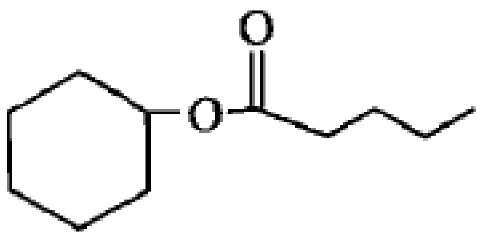
p-toluenesulfonyl chloride

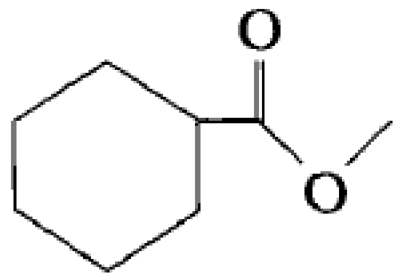


benzoyl chloride

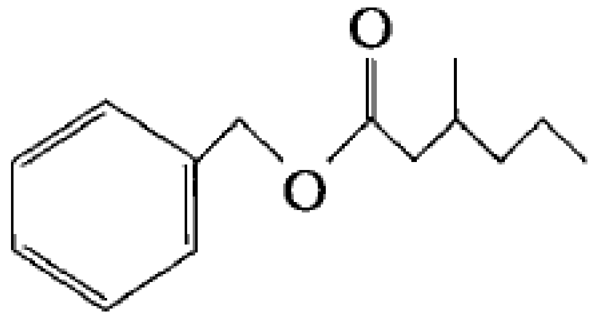
4.13 Nomenclature of Esters

An **ester** is a combination of a carboxylic acid and an alcohol, with loss of a molecule of water. Nomenclature of esters is derived from the names of the carboxylic acids and alcohols from which the esters are derived. An ester name always has two separate words: the name of the alkyl or aryl group derived from the alcohol component is stated first, followed by the name derived from the carboxylic acid, with "**ic acid**" replaced by "**ate**" (the same as for a *carboxylate anion*). The IUPAC name is derived from the IUPAC names of the alkyl or aryl group and the carboxylate, and the common names is derived from the common names of each. Esters of cyclic carboxylic acids are named *alkyl cycloalkanecarboxylates*.

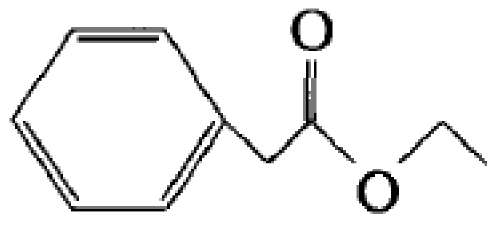
		
IUPAC:	propyl propanoate	ethyl 3-chlorobutanoate
common:	propyl propionate	ethyl β-chlorobutyrate
		
IUPAC:	phenyl ethanoate	cyclohexyl pentanoate
common:	phenyl acetate	cyclohexyl valerate



propyl cyclohexanecarboxylate

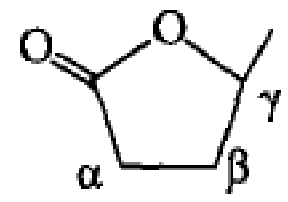


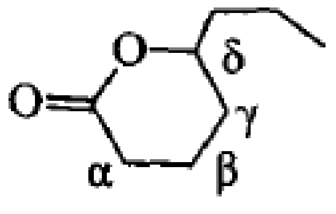
benzyl 3-methylhexanoate

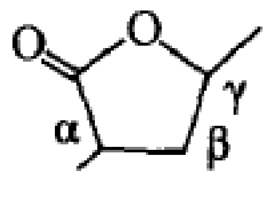


ethyl 2-phenylethanoate

Cyclic esters are called **lactones**. A lactone is formed from an open – chain hydroxy acid in which the hydroxyl group has reacted with the acid group to form an ester. In systematic nomenclature, the ring is named as a cyclic ketone "**2-oxacycloalkanones**". The carbonyl carbon atom is always atom C – 1. The term "**oxa**" is used to name the ring oxygen atom. Their common names are derived from the common name of the carboxylic acid, replacing "**-ic acid**" or "**-oic acid**" by "**-olactone**" and a Greek letter to indicate the carbon to which the carboxyl oxygen is attached. Substituents are named just as they are on the parent acid.





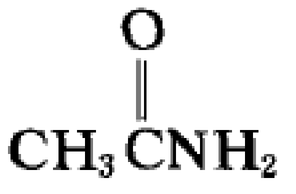


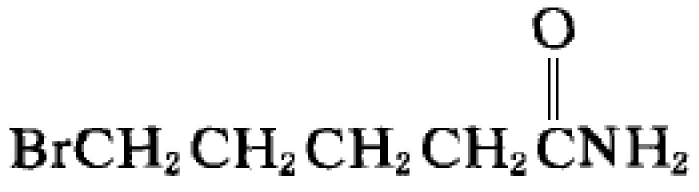
IUPAC:	3-methyl-2-oxacyclopentanone	3-propyl-2-oxacyclohexanone	3,5-dimethyl-2-oxacyclopentanone
common:	γ-valerolactone	δ-caprylolactone	α-methyl-γ-valerolactone

4.14 Nomenclature of Amides

Amides are acid derivatives that result from a combination of an acid with ammonia or an amine. Amides are named by using the carboxylic acid name which the amides are derived, replacing the suffix "**oic acid**" of IUPAC names or the suffix "**ic acid**" of common names with "**amide**". For cyclic carboxylic acids ending with "**carboxylic acid**", "**ylic acid**" is replaced with "**amide**".

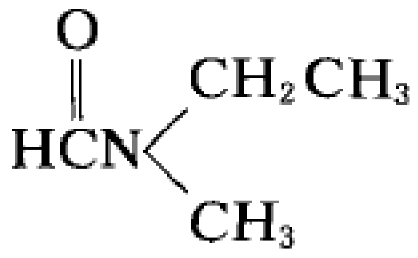
If an alkyl or aryl is bonded to the nitrogen, the alkyl or aryl group is indicated by a capital *N* preceding the alkyl or aryl group name. If there is more than one substituent bonded to the nitrogen, they are listed alphabetically and the name of each substituent is preceded by a capital *N*, followed by the name of the amide.


$CH_3\overset{\overset{O}{\|}}{C}NH_2$

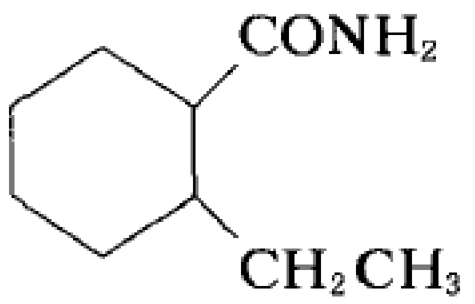

$BrCH_2CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2$


$CH_3\overset{\overset{O}{\|}}{C}NHCH_2CH_3$

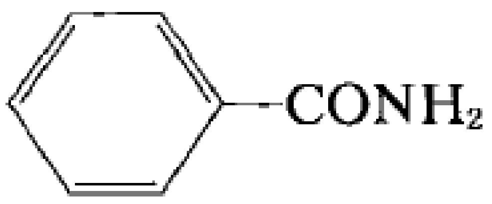
IUPAC:	ethanamide	5-bromopentanamide	*N*-ethylethanamide
common:	acetamide	δ-bromovaleramide	*N*-ethylacetamide



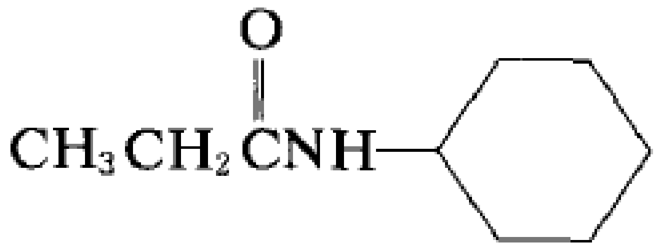
IUPAC: *N*-ethyl-*N*-methylmethanamide
common: *N*-ethyl-*N*-methylformamide



2-ethylcyclohexanecarboxamide



benzamide

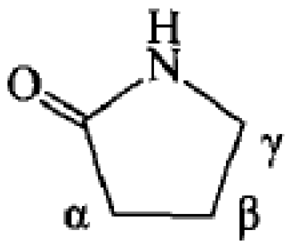


N-cyclohexylpropanamide

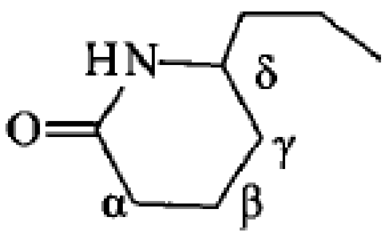
N,*N*-dimethylcyclobutanecarboxamide

Cyclic amides are called **lactams**. The nitrogen atom is one of the ring atoms. Lactams are made by an intramolecular condensation reaction between amine and carboxylic acid functional groups. Their nomenclature is similar to that of lactones. They are named as "**2-azacycloalkanones**" in systematic nomenclature. The ring is named as a cyclic ketone and the nitrogen atom is designated by "**aza**". The carbonyl carbon atom is atom number one and the nitrogen atom is number two in the ring.

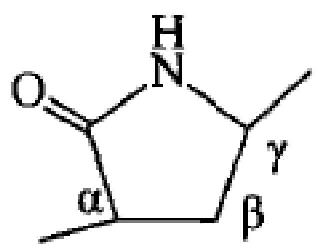
The common name for a lactam is derived from the common name of the corresponding amino acid by dropping the word amino and replacing the "**-ic acid**" or "**-oic acid**" by "**-olactam**". The length of the carbon chain is indicated by the common name of the carboxylic acid and a Greek letter indicates the carbon to which the nitrogen is attached. The α -carbon is adjacent to the carbonyl group.



IUPAC: 2-azacyclopentanone
common: γ-butyrolactam



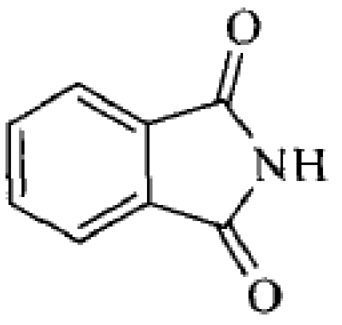
3-propyl-2-azacyclohexanone
δ-caprylolactam



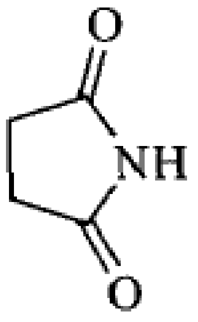
3,5-dimethyl-2-azacyclopentanone
α-methyl-γ-valerolactam

An **imide** is a compound with two acyl groups bonded to a nitrogen. The common name of imides is based on the parent carboxylic acid. The suffix "**-ic acid**" is dropped and "**imide**" is added. Phthalic acid becomes *phthalimide*.

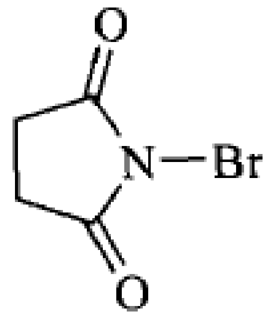
Succinic acid becomes *succinimide*.



phthalimide



succinimide

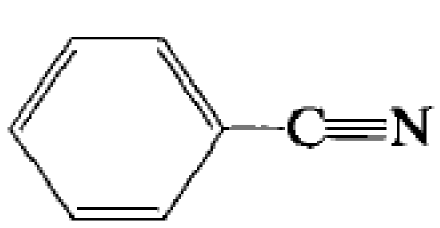
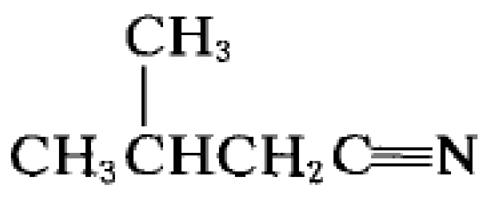


N-bromosuccinimide (NBS)

4.15 Nomenclature of Nitriles

Nitriles are compounds that contain a **—C≡N** functional group. Nitriles are considered carboxylic acid derivatives because they react with water to form carboxylic acids. In systematic nomenclature, nitriles are named by adding **"nitrile"** to the parent alkane name. It is important to count all of the carbon atoms in the longest continuous chain, even if one of them is part of a —C≡N functional group, so *pentanenitrile* is actually BuCN. The carbon atom in the nitrile group is always atom number one in the alkane segment.

In common nomenclature, the common name for nitriles is derived from the common name of the carboxylic acid that results from hydrolysis of the nitrile. Nitriles are named by replacing the suffix **"-ic acid"** or **"-oic acid "** of the carboxylic acid name with **"onitrile"**. They can also be named as **alkyl cyanides** (the C≡N anion is called a **cyanide ion**), stating the name of the alkyl group that is attached to the —C≡N group.

	$H_3C—C≡N$	$H_2C=CH—C≡N$		 $CH_3\overset{CH_3}{\overset{\vert}{C}H}CH_2C≡N$
IUPAC:	ethanenitrile	propenenitrile	benzenecarbonitrile	3-methylbutanenitrile
common:	acetonitrile	acrylontrile	benzonitrile	β-methylbutyronitrile
	methyl cyanide	ethenyl cyanide	phenyl cyanide	isobutyl cyanide

4.16 Nomenclature of Amines

Amines are compounds in which one or more of the hydrogens of ammonia have been replaced by alkyl groups. There are primary amines, secondary amines and tertiary amines. The classification depends on how many alkyl groups are bonded to the nitrogen. Primary amines have one alkyl group bonded to the nitrogen, secondary amines have two, and tertiary amines have three. Any compound whose name has the suffix "**-ine**" is an amine, even most commercial products with trade names. For example, caffeine, nicotine, and Benzedrine are all amines.

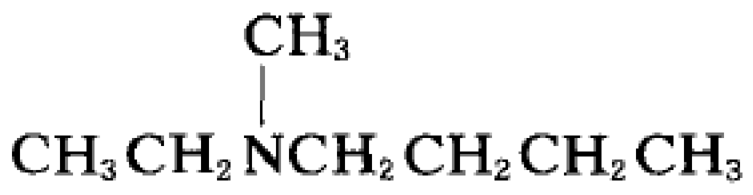
The common name of an amine consists of the names of the alkyl groups attached to the nitrogen, in alphabetical order, followed by the suffix "**amine**". Two or three identical groups are designated by the prefixes "**di-**" and "**tri-**". The entire name is written as one word (unlike the common names of alcohols, ethers, and alkyl halides, in which "**alcohol**", "**ether**", and "**halide**" are separate words).

CH_3NH_2

methylamine

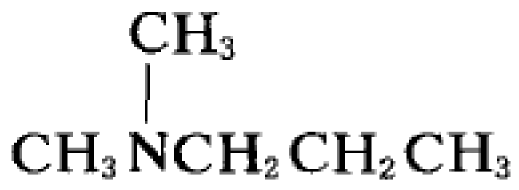
$CH_3CH_2NHCH_2CH_2CH_2CH_3$

butylethylamine



$CH_3CH_2\overset{\overset{CH_3}{|}}{N}CH_2CH_2CH_2CH_3$

butylethylmethylamine

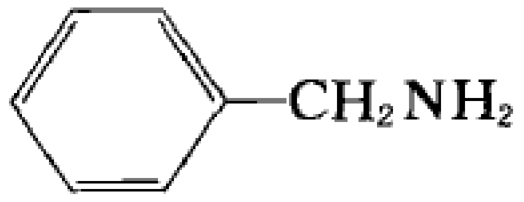


$CH_3\overset{\overset{CH_3}{|}}{N}CH_2CH_2CH_3$

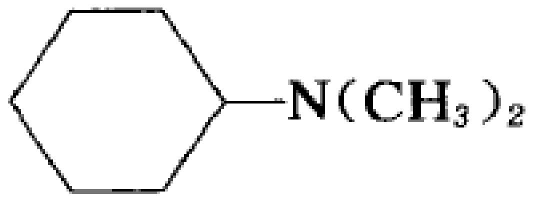
dimethylpropylamine

$CH_3CH_2CH_2NHCH_2CH_2CH_3$

dipropylamine



benzylamine



cyclohexyldimethylamine

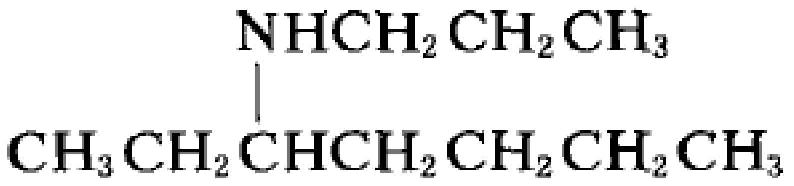
The IUPAC system uses a suffix to denote the amine functional group. The "**e**" at the end of the name of the longest straight chain of carbon atoms attached to the nitrogen is replaced by "**amine**"—similar to the way in which alcohols are named. The chain is numbered in the direction that gives the amine functional group suffix the lowest possible number. A number identifies the carbon to which the nitrogen is attached. The number can appear before the name of the parent hydrocarbon or before "**amine**", and the prefix "**N－**" is used for each substituent on nitrogen to indicate that the group is bonded to a nitrogen rather than to a carbon. Other substituents on the carbon chain are designated in the usual manner (name of group and position number). The substituents are listed in alphabetical order with a number or an "*N*" assigned to each one.

$CH_3CH_2CH_2NH_2$

1-propanamine

or

propan − 1 − amine

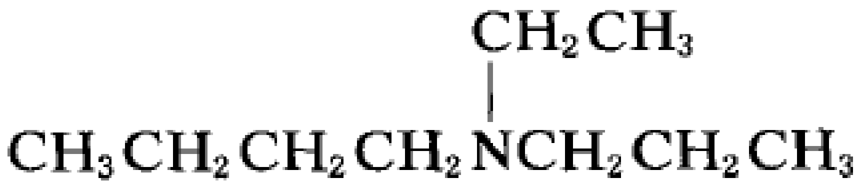


$$CH_3CH_2\overset{\overset{\displaystyle NHCH_2CH_2CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$$

N-propyl-3-heptanamine

or

N-propylheptan-3-amine

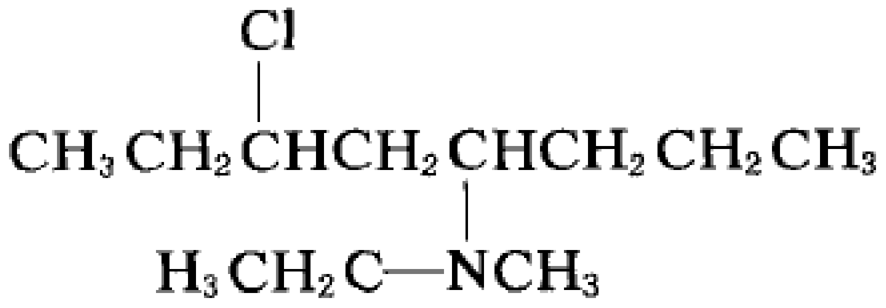


$$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{N}CH_2CH_2CH_3$$

N-ethyl-*N*-propyl-1-butanamine

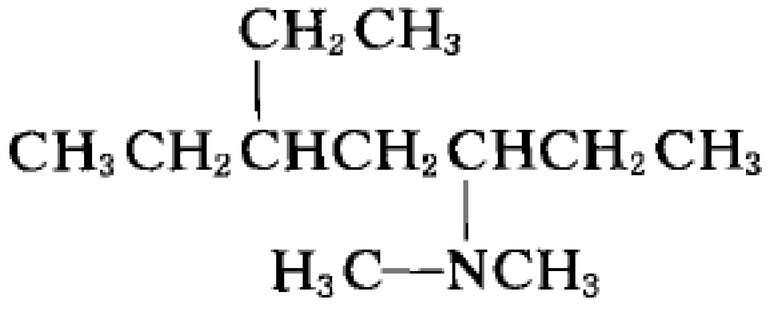
or

N-ethyl-*N*-propylbutan-1-amine



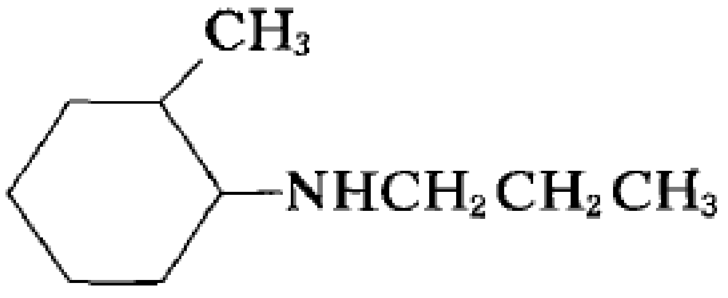
$$CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{C}HCH_2\underset{\underset{\displaystyle H_3CH_2C{-}NCH_3}{|}}{C}HCH_2CH_2CH_3$$

6-chloro-*N*-ethyl-*N*-methyl-4-octanamine

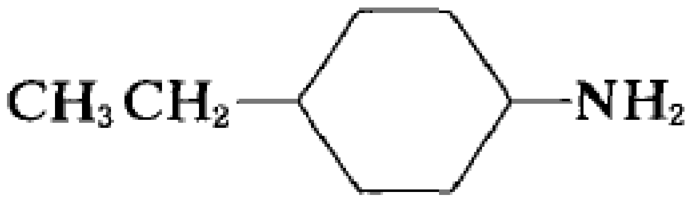


$$CH_3CH_2\overset{\overset{\displaystyle CH_2CH_3}{|}}{C}HCH_2\underset{\underset{\displaystyle H_3C{-}NCH_3}{|}}{C}HCH_2CH_3$$

5-ethyl-*N*, *N*-dimethyl-3-heptanamine

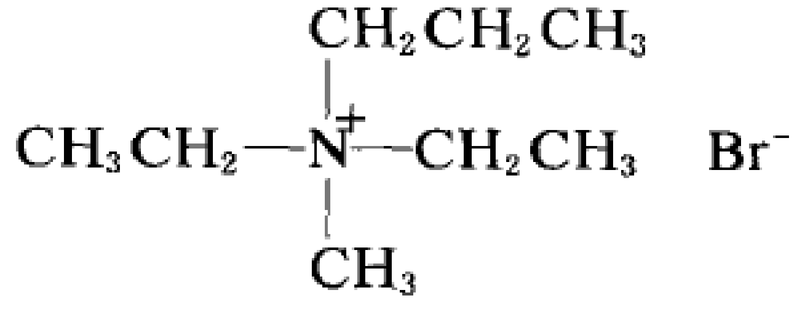


2-methyl-*N*-propylcyclohexanamine



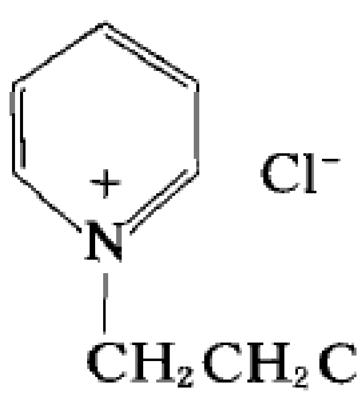
4-ethylcyclohexanamine

Nitrogen compounds with four alkyl groups bonded to the nitrogen (the nitrogen atom bears a positive charge) are called **quaternary ammonium salts.** Their names consist of the names of the alkyl groups in alphabetical order, followed by "**ammonium**" (all in one word), and then the name of the counterion as a separate word.

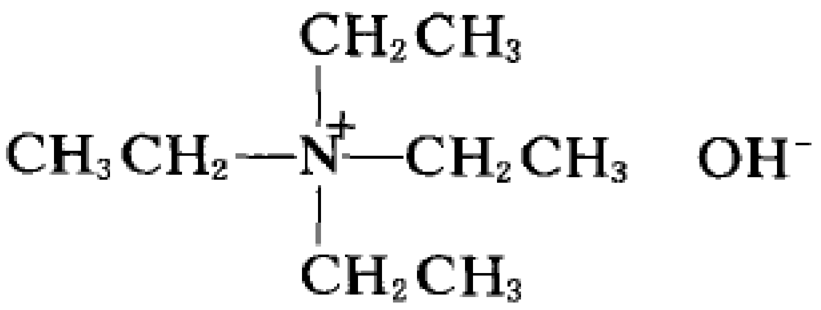


$$CH_3CH_2-\overset{\displaystyle CH_2CH_2CH_3}{\underset{\displaystyle CH_3}{\overset{+}{N}}}-CH_2CH_3\quad Br^-$$

N,*N*-diethyl-*N*-methylpropan-1-ammonium bromide



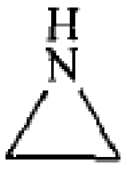
N-propylpyridinium chloride



$$CH_3CH_2-\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_2CH_3}{\overset{+}{N}}}-CH_2CH_3\quad OH^-$$

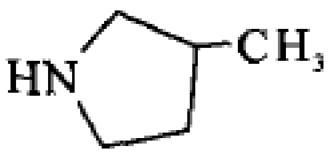
tetraethylammonium hydroxide

A **cyclic amine** without any double bonds can be named as a **cycloalkane**, using the prefix "**aza**" to denote the nitrogen atom, and heterocyclic rings are numbered so that the heteroatom has the lowest possible number. Some of the more commonly used names are shown here.

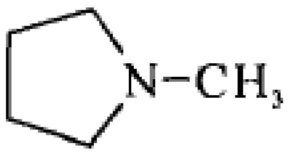


azacyclopropane
aziridine

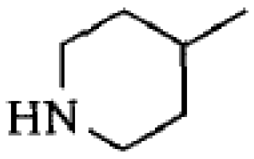
azacyclobutane
azetidine



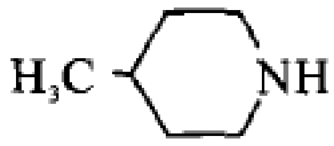
3-methylazacyclopentane
3-methyplyrrolidine



N-methylazacyclopentane
N-methylpyrrolidine

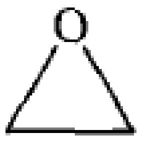


4-methylazacyclohexane



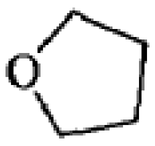
4-methylpiperidine

Heterocycles with oxygen and sulfur heteroatoms are named similarly. The prefix for **oxygen** is "**oxa**" and that for **sulfur** is "**thia**".

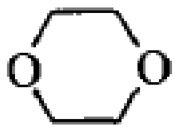


oxacyclopropane
oxirane
ethylene oxide

oxacyclobutane
oxetane



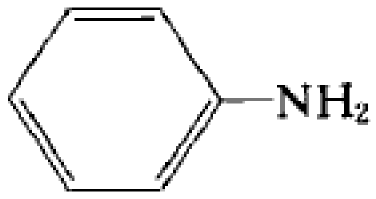
oxacyclopentane
tetrahydrofuran



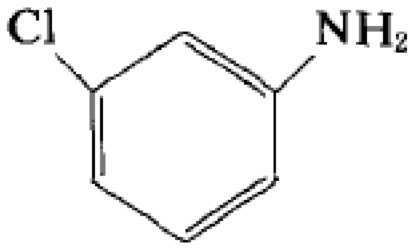
1,4-dioxane

thiacyclopropane
thiirane

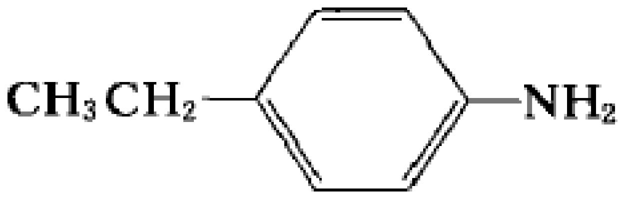
Phenylamine is called **aniline** and **benzenoid amines** are named as derivatives of aniline.



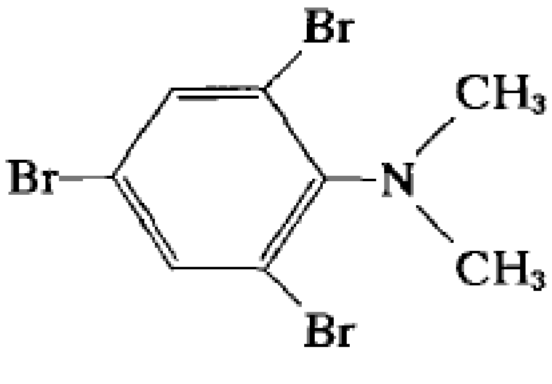
aniline



m-chloroaniline

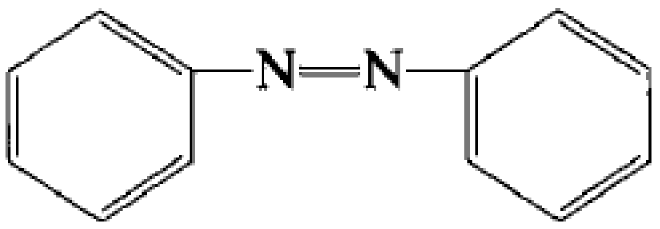


p-ethylaniline

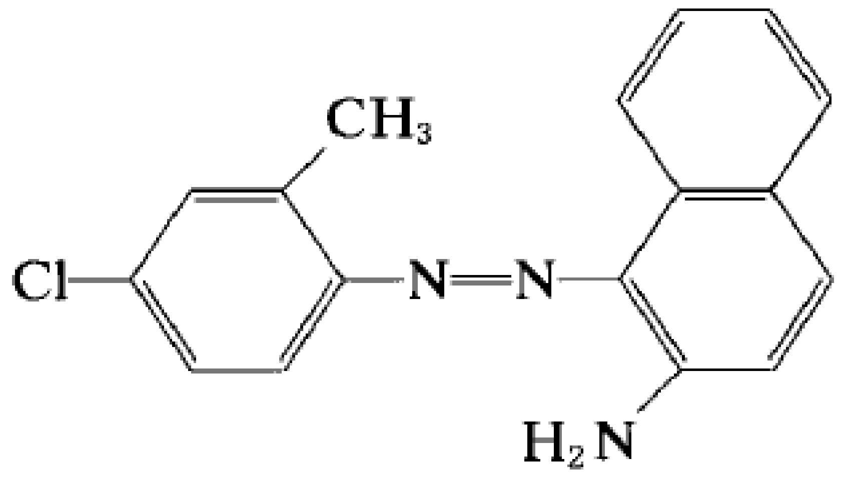


N,*N*-dimethyl-2,4,6-tribromoaniline

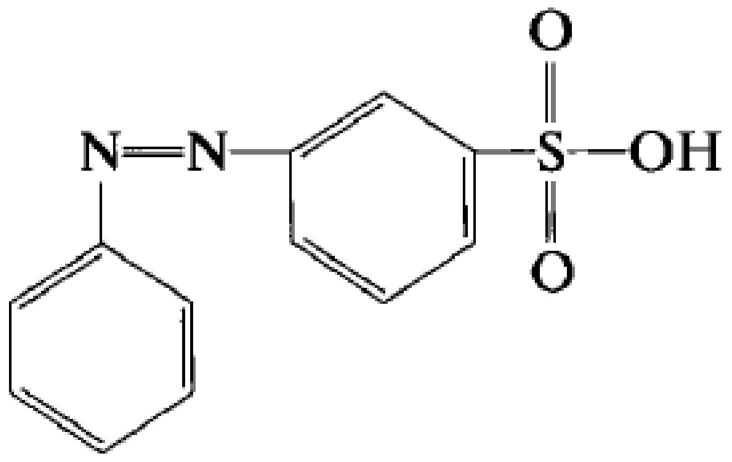
When the **azo** group (—N=N—) connects radicals derived from identical unsubstituted molecules, the name is formed by adding the prefix **azo**- to the name of the parent unsubstituted molecules. Substituents are denoted by prefixes and suffixes. The **azo** group has priority for lowest-numbered locant. When the parent molecules connected by the azo group are different, **azo** is placed between the complete names of the parent molecules, substituted or unsubstituted. Locants are placed between the affix **azo** and the names of the molecules to which each refers. Preference is given to the more complex parent molecule for citation as the first component.



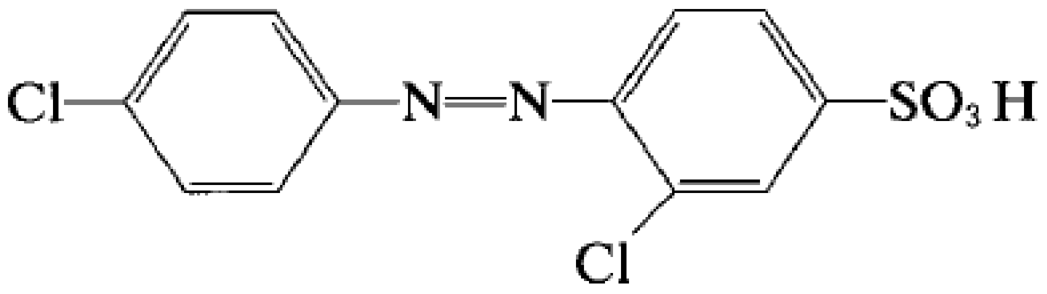
azobenzene



2-aminonaphthalene-1-azo-(4′-chloro-2′-methylbenzene)



azobenzene-4-sulfonic acid



2′,4-dichloroazobenzene-4′-sulfonic acid

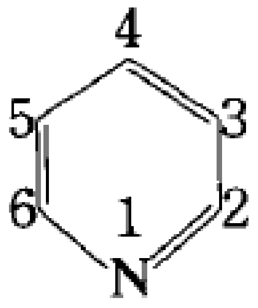
4.17 Nomenclature of Heterocyclic Compounds

A **heterocyclic** molecule is a cyclic compound in which one or more of the atoms in the ring is a heteroatom. Within organic chemistry, the heteroatom is an atom other than carbon or hydrogen, and common heteroatoms are N, O and S. A heterocycle can be saturated (e.g. tetrahydrofuran, THF), unsaturated (e.g. pyran) or aromatic (e.g. pyridine). The aromatic heterocycles have been grouped into those with six-membered rings and those with five-membered rings. A large proportion of naturally occurring organic compounds are heterocyclic, and many are of biological importance. For this reason, we need to be familiar with the large number of ring types and the corresponding array of names for parent heterocyclic rings.

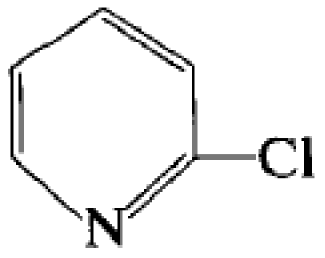
A selection of the structures, names and standard numbering of the more common heteroaromatic systems and some common non-aromatic heterocycles are given here.

The names of six-membered aromatic heterocycles that contain nitrogen generally end in "**ine**", though note that "**purine**" is the name for a very important bicyclic system which has both a six- and a five-membered nitrogen-containing heterocycle. Five-membered heterocycles containing nitrogen general end with "**ole**".

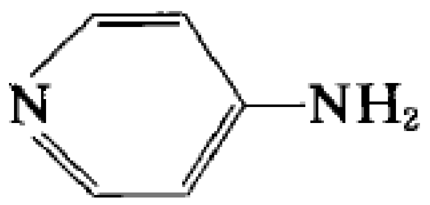
In monocyclic systems containing one heteroatom, ring atom numbering begins at the heteroatom, and derivatives are named by using the position of substitution, for example:



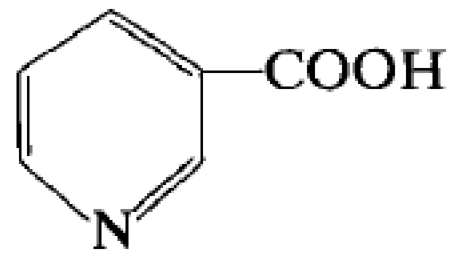
pyridine



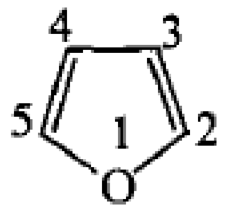
2-chloropyridine



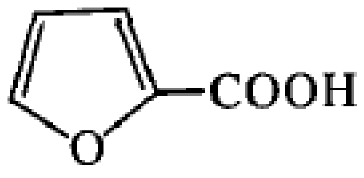
4-aminopyridine



pyridine-3-carboxylic acid

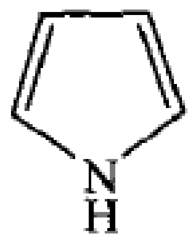


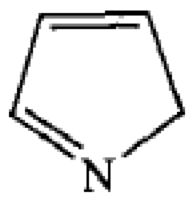
furan



furan-2-carboxylic acid

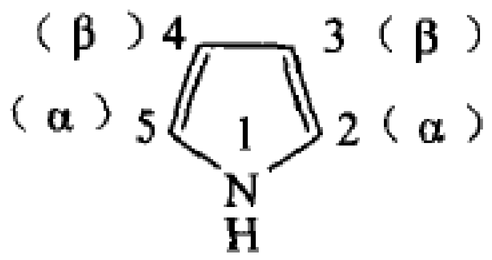
Names such *pyridine*, *pyrrole*, *thiophene*, originally trivial, are now the standard, systematic names for these heterocycles, names such as *1,2,4-triazine* for a six-membered ring with three nitrogens located as indicated by the numbers, are more logically systematic. In some cases, heterocyclic systems occur as one or more structural isomers which differ only in the position of an **H-atom**. These isomers are designated by indicating the number corresponding to the position of the hydrogen atom in front of the name, followed by an italic capital ***H***. Such a prominent H-atom is called an **indicated hydrogen** and must be assigned the lowest possible locant.


1*H*-pyrrole

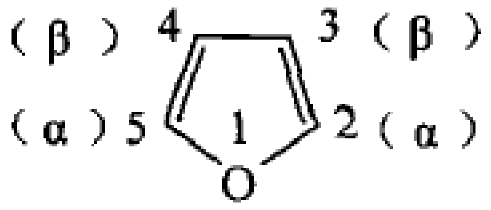

2*H*-pyrrole


3,4-dihydro-2*H*-pyrrole

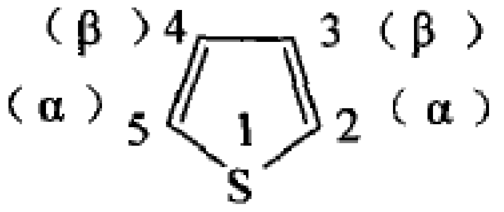
Ring numberings for several other important molecules are given below for reference. In fused ring systems, the heteroatom is not necessarily at position 1. Note that **carbons at angular positions** do not have a separate number, but are designated using the number of the preceding atom followed by "**a**". For historical reasons purine does not follow this rule.



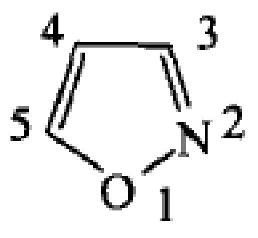
pyrrole



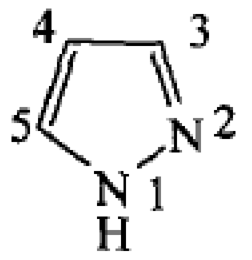
furan



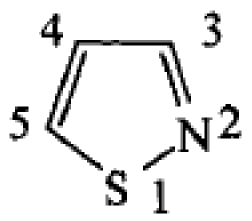
thiophene



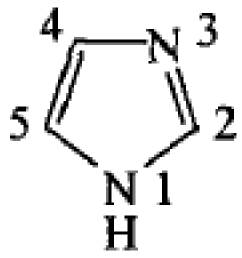
isoxazole



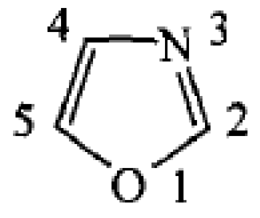
pyrazole



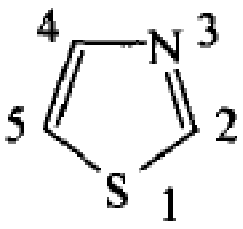
isothiazole



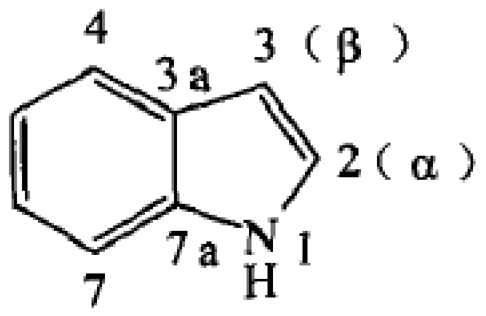
imidazole



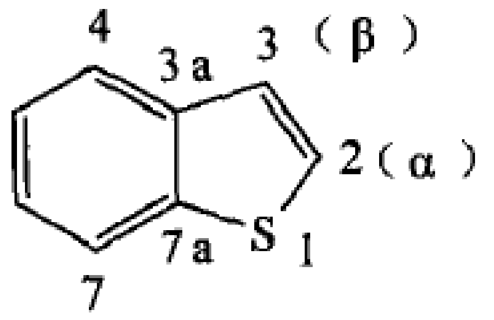
oxazole



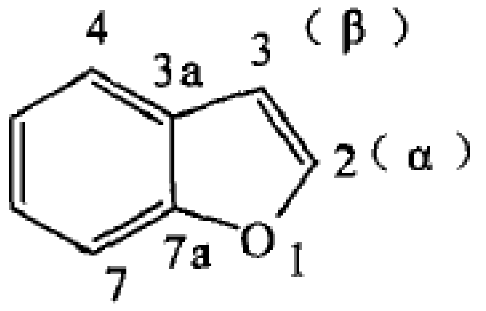
thiazole



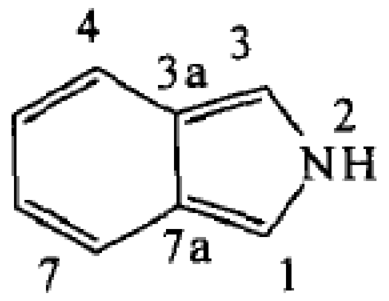
1*H*-indole



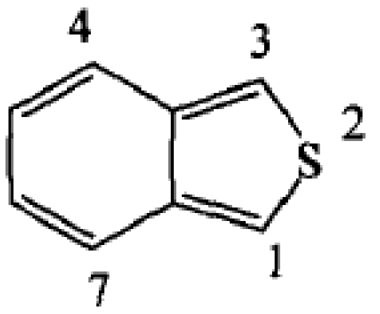
benzo[*b*]thiophene



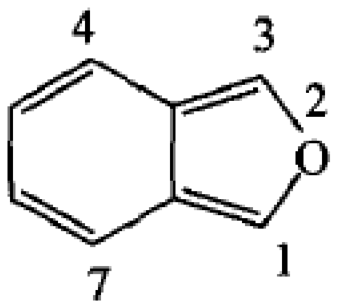
benzo[*b*]furan



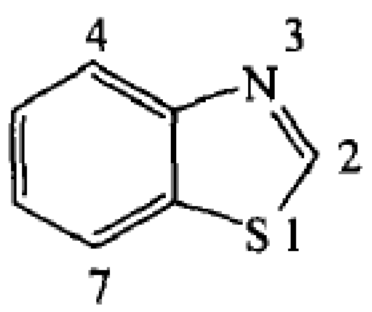
2*H*-isoindole



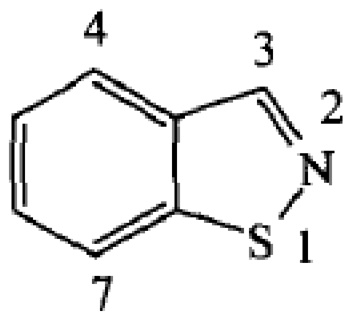
benzo[*c*]thiophene



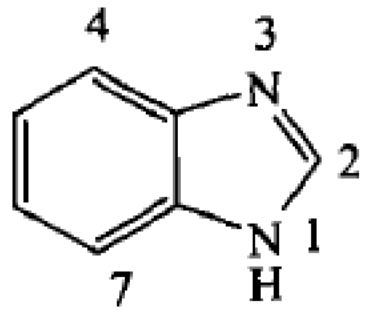
isobenzofuran



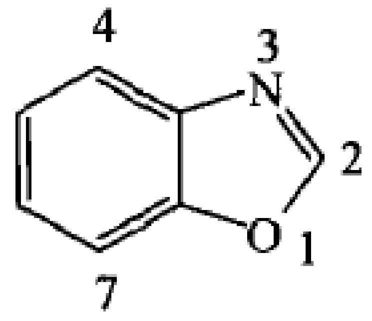
benzothiazole



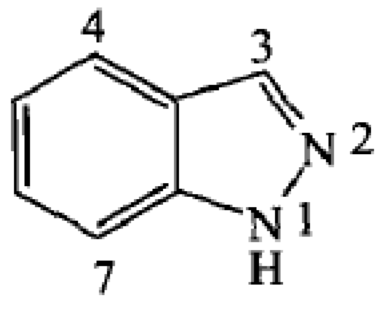
1,2-benzisothiazole



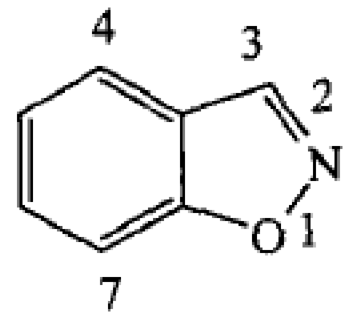
1*H*-benzo[*d*]imidazole



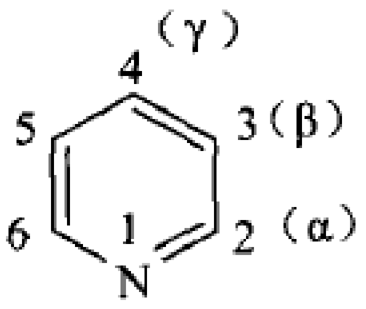
benzoxazole



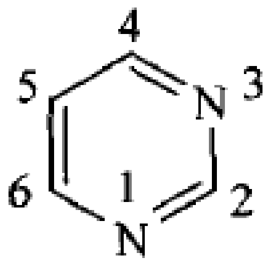
1*H*-indazole



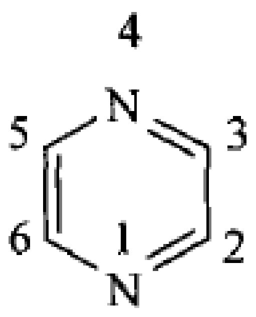
1,2-benzisoxazole



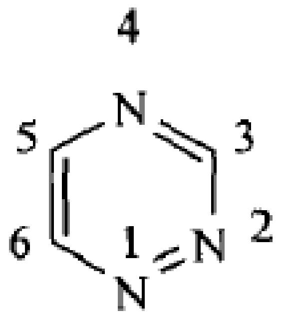
pyridine



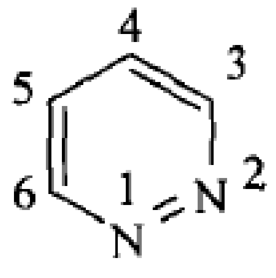
pyrimidine



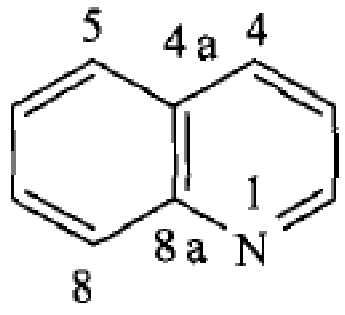
pyrazine



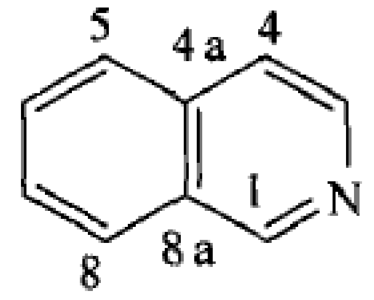
1,2,4-triazine



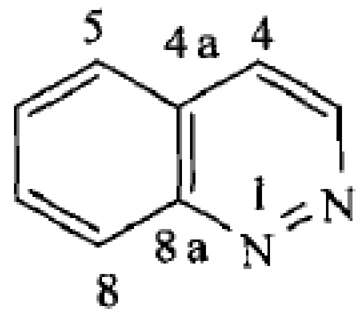
pyridazine



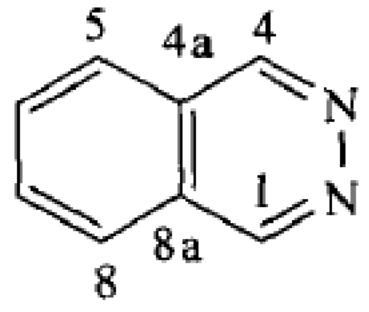
quinoline



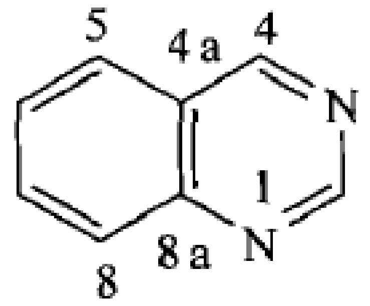
isoquinoline



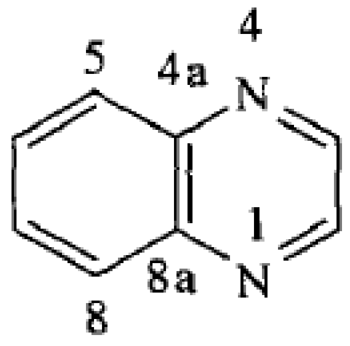
cinnoline



phthalazine



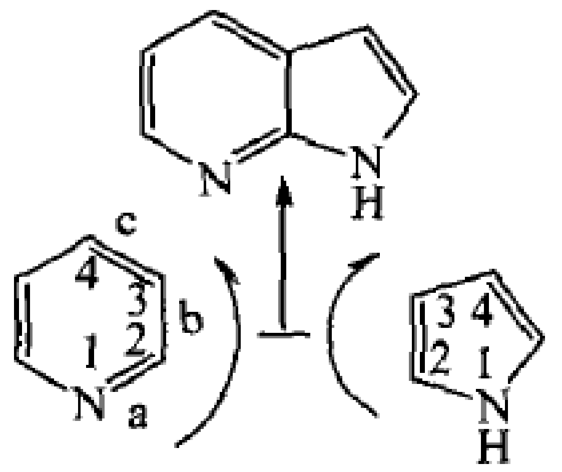
quinazoline



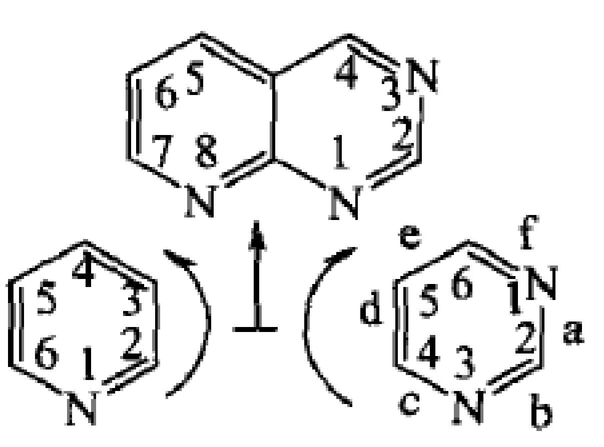
quinoxaline

A device that is useful, especially in discussions of reactivity, is the designation of positions as "**α**", "**β**" or "**γ**" . For example, the 2-and the 6-positions in pyridine are equivalent in reactivity terms, to make discussion of such reactivity clearer, each of these positions is referred to as an "α-position". Comparable use of α and β is made in describing reactivity in five-membered systems. These useful designations are shown on some of the structures.

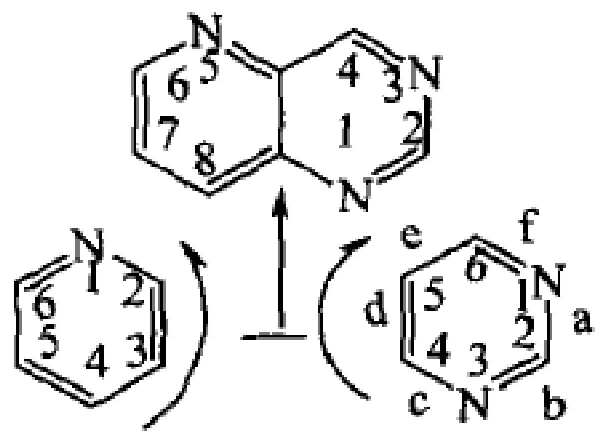
A simple example will serve to illustrate the principle for **naming polycyclic systems** in which several aromatic or heteroaromatic rings are fused together. In the name "**pyrrolo[2,3-*b*]pyridine**", the numbers signify the positions of the first-named heterocycle, numbered as if it were a separate entity, which are the points of ring fusion; the italic letter, "***b***" in this case, designates the side of the second-named heterocycle to which the other ring is fused, the lettering deriving from the numbering of that heterocycle as a separate entity, i.e. **side *a*** is between atoms 1 and 2, **side *b*** is between atoms 2 and 3, etc. Actually, this particular heterocycle is more often referred to as "7 - azaindole" - note the use of the prefix "**aza**" to denote the replacement of a ring carbon by nitrogen, i.e. of C-7 - H of indole by N.



pyrrolo[2,3-*b*]pyridine
(7-azaindole)



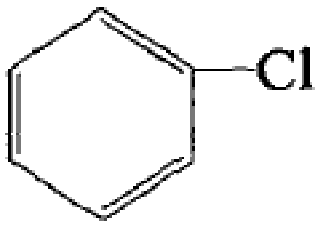
pyrido[2,3-*d*]pyrimidine



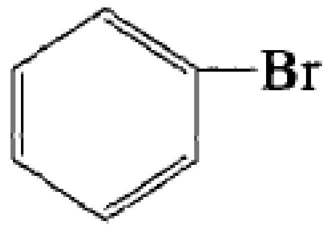
pyrido[3,2-*d*]pyrimidine

4.18 Nomenclature of Benzenoid Compounds

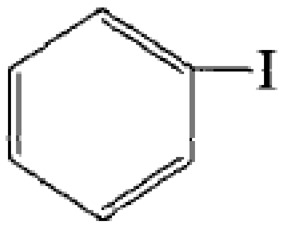
Compounds in which another substituent has replaced a single hydrogen of benzene are called **monosubstituted benzenes**. IUPAC nomenclature designates them as substituted benzenes. It is not necessary to state the location of the substituent in a monosubstituted benzene. Some derivatives have special names which may show no resemblance to the name of the attached substituent group.



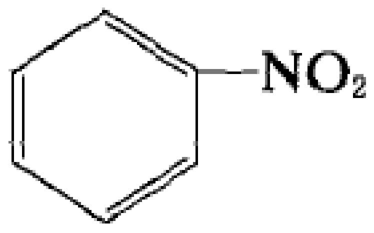
IUPAC: chlorobenzene



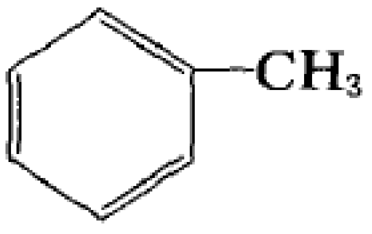
bromobenzene



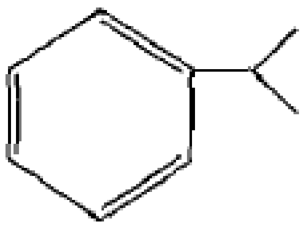
iodobenzene



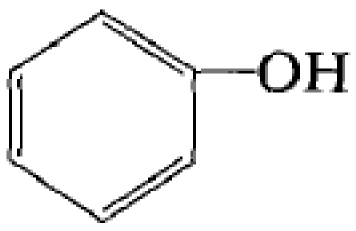
nitrobenzene



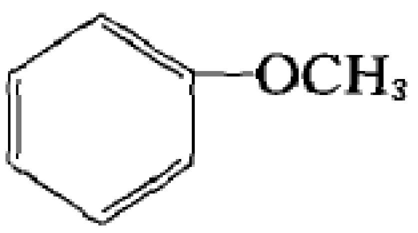
IUPAC: methylbenzene
common: toluene



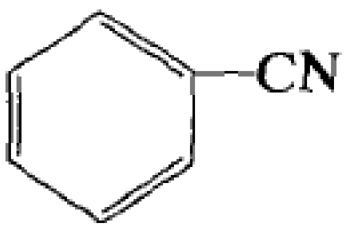
isopropylbenzene
cumene



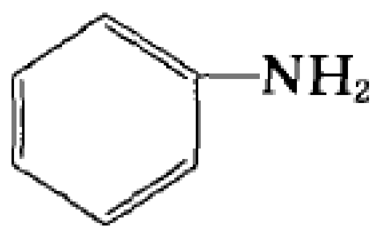
hydroxybenzene
phenol



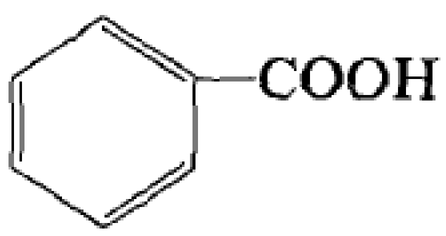
methoxybenzene
anisole



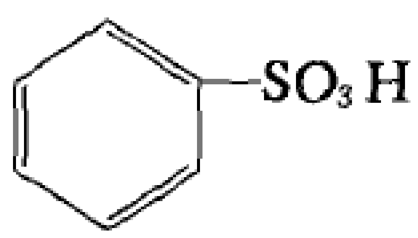
IUPAC: cyanobenzene
common: benzonitrile



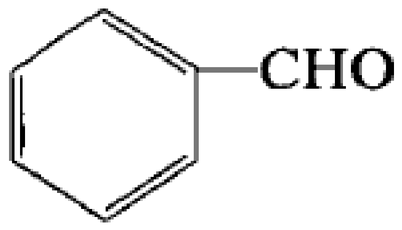
aminobenzene
aniline



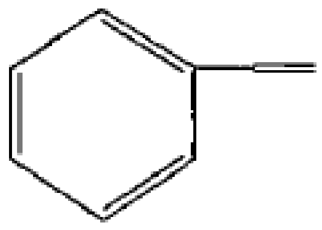
benzoic acid



benzenesulfonic acid



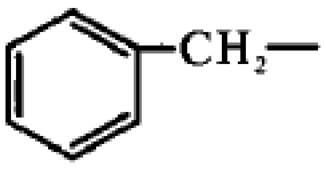
common: benzaldehyde



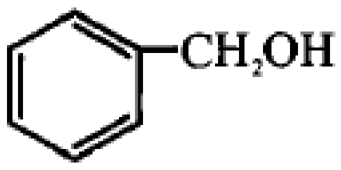
styrene

Any benzene substituted by an aliphatic group may be named as **alkyl-substituted benzenes** or as **phenyl-substituted alkanes**. If the benzene ring is considered a substituent, it is called a phenyl group. The phenyl group, **Ph**, is used in the name just like the name of an alkyl group, and it is often abbreviated Ph in drawing a complex structure. A **benzene ring with a methylene** group is called a **benzyl group**. Be careful not to confuse the **benzyl group** (seven carbons) with the **phenyl group** (six carbons).

a phenyl group

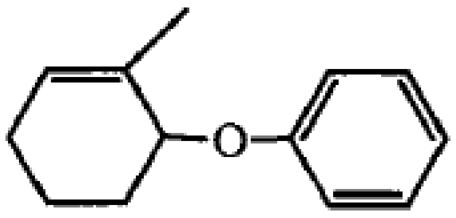


a benzyl group

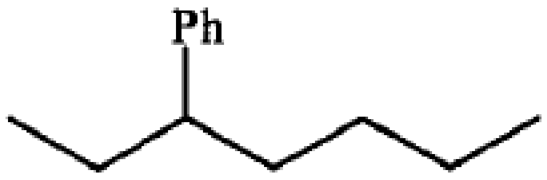


benzyl alochol

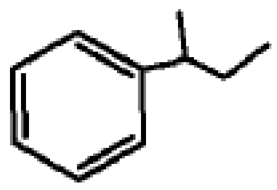
1-phenylpent-1-yne



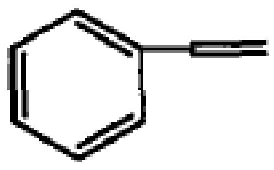
2-methyl-3-phenoxycyclohexene



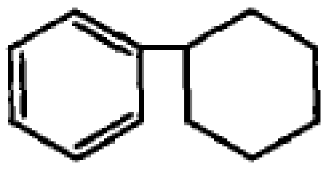
3-phenylheptane



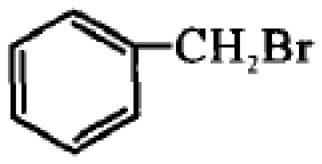
sec-butylbenzene
2-phenylbutane



vinylbenzene
phenylethene



cyclohexylbenzene
phenylcyclohexane

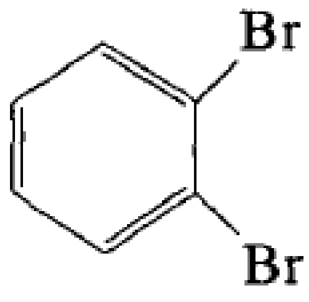


bromomethylbenzene
benzylbromide

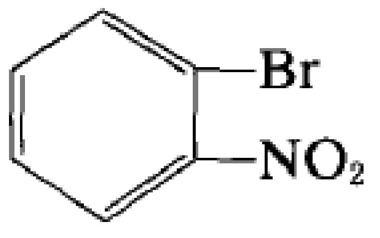
Aromatic hydrocarbons are sometimes called **arenes**. The generalized designation for an aromatic group that remains after the removal of a hydrogen atom from an aromatic ring is **Ar—** (short for aryl group). An **aryl group** is the general term for either a phenyl group or a substituted phenyl group, The phenyl group is the simplest aryl group. **Ar-R** represents an **alkylaromatic** compound.

Two substituents on a benzene ring may occupy three different sets of relative positions. The positions of the substituents in disubstituted benzenes can be on carbon atoms C-1 and C-2, C-1 and C-3, C-1 and C-4. The three possible isomers of a disubstituted benzene are differentiated by the use of the prefix names ***ortho*** (***o***), ***meta*** (***m***), and ***para*** (***p***). Numbers can also be used to specify the substitution in disubstituted benzenes.

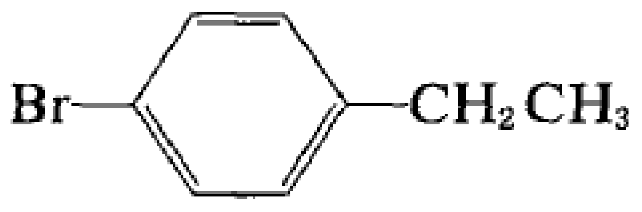
If the two substituents are identical, the prefix **di-** is used. If the two groups are different, and neither is a group that gives a special name to the molecule, they are listed in alphabetical order, and end the word with **-benzene**. The first stated substituent is given the 1 – position, and the ring is numbered in the direction that gives the second substituent the lowest possible number.



o-dibromobenzene
1,2-dibromobenzene

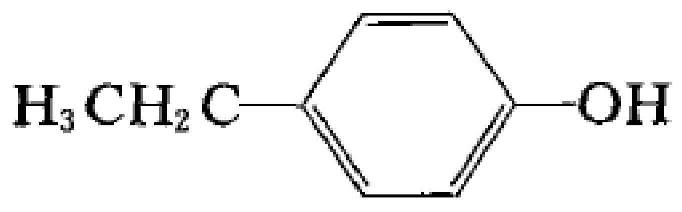


o-bromonitrobenzene
1-bromo-2-nitrobenzene

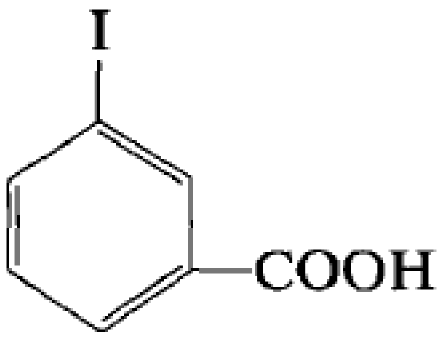


p-bromoethylphenzene
1-bromo-4-ethylbenzene

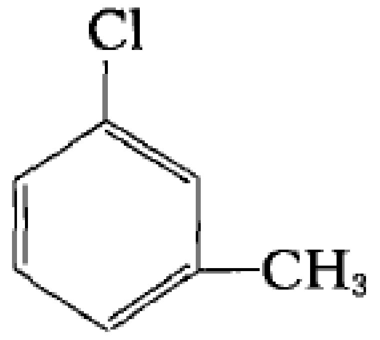
If one of the two groups is the kind that gives a special name to the molecule, that name is used and the incorporated substituent is given the 1-position.



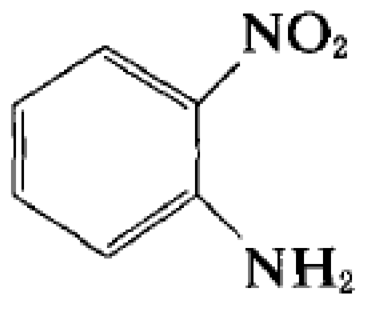
p-ethylphenol
4-ethylphenol



m-iodobenzoic acid
3-iodobenzoic acid

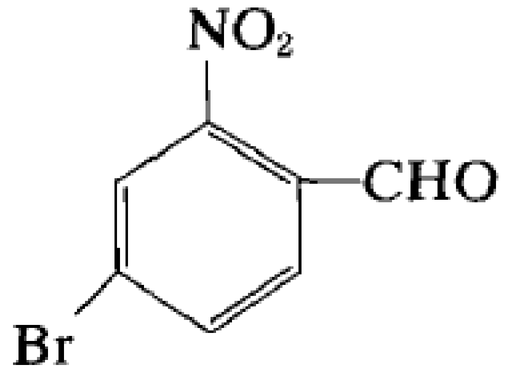


m-chlorotoluene
3-chlorotoluene

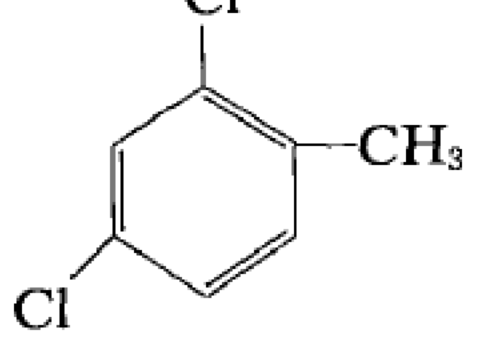


o-nitroaniline
2-nitroaniline

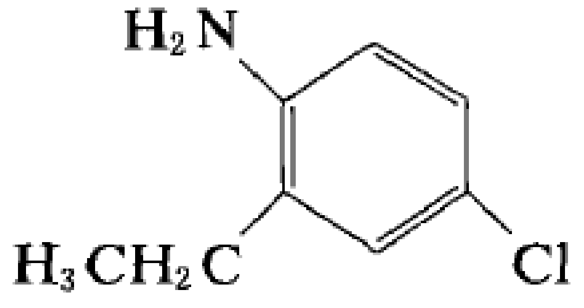
If there are three or more substituents, numbers are assigned to the substituents to give the lowest number combination. First, a parent name is chosen based on one of the substituents, which determines position 1. Then the ring is numbered in the direction that results in the lowest possible numbers in the name of the compound. The substituents are named in alphabetical order, not numerical order.



4-bromo-2-nitrobenzaldehyde

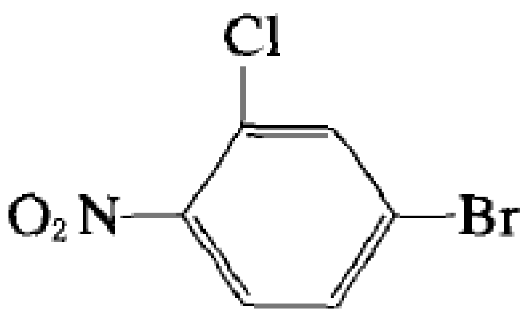


2,4-dichlorotoluene

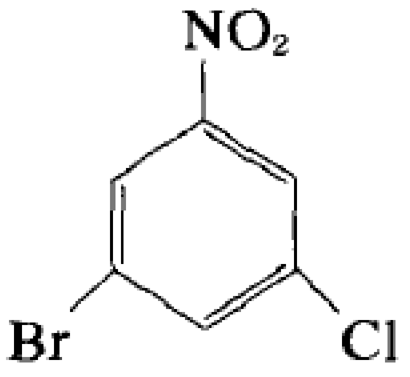


4-chloro-2-ethylaniline

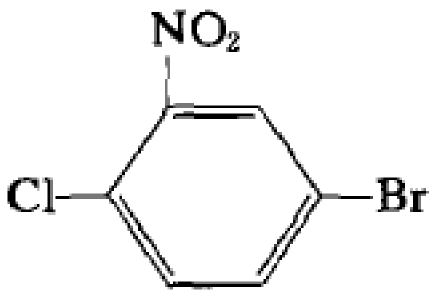
If the groups are different and no special name is present, then the last-named group is understood to be in position 1 and the sequence being the one that gives the lowest combination of numbers.



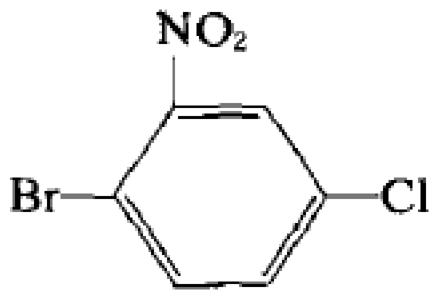
4-bromo-2-chloro-1-nitrobenzene



3-bromo-5-chloro-1-nitrobenzene

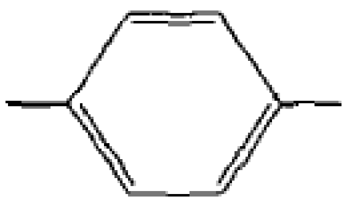


4-bromo-1-chloro-2-nitrobenzene

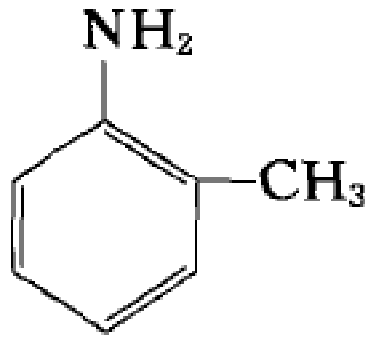


1-bromo-4-chloro-2-nitrobenzene

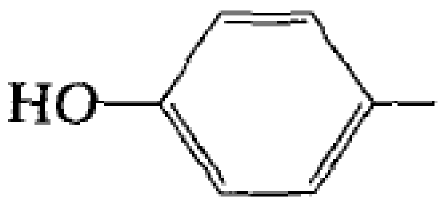
Many polysubstituted benzenes have historical names with no obvious connection to the structure of the molecule.



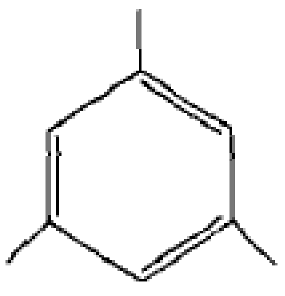
p-xylene
1,4-dimethylbenzene



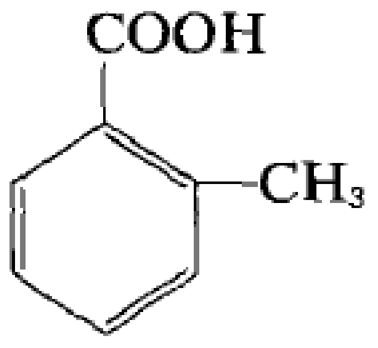
o-toluidine
2-methylaniline



p-cresol
4-methylphenol



mesitylene
1,3,5-trimethylbenzene



o-toluic acid
2-methylbenzoic acid

4.19 Nomenclature of Polyfunctional Compounds

How should IUPAC names be derived for compounds containing more than one functional group? If there is more than one functional group in a molecule, there is a hierarchy for assigning the parent. The hierarchy order, highest to lowest, is: carboxylic acid, ester, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, alkene, alkyne, alkane, ether, and halide (see Table 4.5). The highest priority group present is the parent in the name.

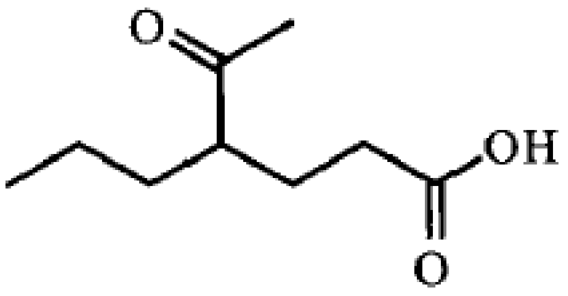
Table 4.5 Precedence of prefixes and suffixes used to designate functional groups

Functional group	Structure	Suffix (when highest precedence)	Prefix (when lower precedence)
Carboxylic acid	$\mathrm{-COOH}$ $\mathrm{C(=O)OOH}$	oic acid or carboxylic acid peroxy ... oic acid or peroxy ... carboxylic acid	Carboxy
Sulfonic	$\mathrm{-SO_3H}$	sulfonic acid	Sulfo
Anhydrides	$\mathrm{-C(=O)OC(=O)-}$	oic anhydride carboxylic anhydride	
Ester	$\mathrm{-COOR}$	oate	Alkoxycarbonyl
Amide	$\mathrm{-CONH_2}$	amide	Amido
Hydrazides	$\mathrm{-CONHNH_2}$	carbohydrazide ohydrazide	Carbonyl-hydrazino
Nitrile	$\mathrm{-CN}$	nitrile	Cyano
Aldehyde	$\mathrm{-CHO}$	al or carbaldehyde	Formyl Oxo
Ketone	$\mathrm{-CO-}$	one	Oxo
Alcohol	$\mathrm{-OH}$	ol	Hydroxy
Amine	$\mathrm{-NH_2}$	amine	Amino
Imines	$\mathrm{=NH}$	imine	Imino

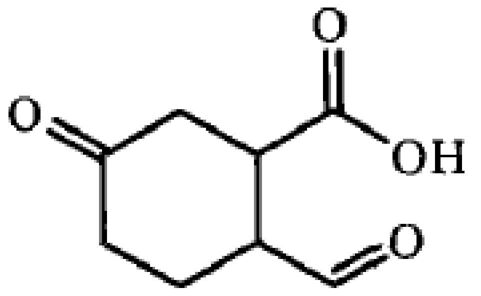
Continued

Functional group	Structure	Suffix (when highest precedence)	Prefix (when lower precedence)
Hydrazines	$-NHNH_2$	hydrazine	Hydrazino
Alkene	$C=C$	ene	Alkenyl
Alkyne	$C\equiv C$	yne	Alkynyl
Alkane	$-R$	ane	Alkyl
Ether	$-OR$		Alkoxy
Sulfides	$-SR$		Alkthio
Alkyl halide	$-X$		Halo

If a compound contains a carboxylic acid and a ketone group, the compound would be named as an acid and the ketone oxygen atom would be named as a substituent.



5-oxo-4-propylhexanoic acid

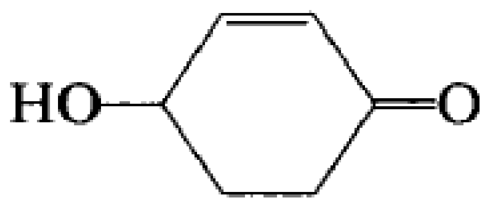


2-formyl-5-oxocyclohexanecarboxylic acid

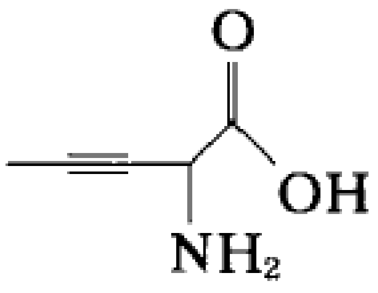
Here are the rules for determining the nomenclature of compounds that contain more than one principal functional group:

First, determine the order of precedence of the functional groups included in the compound (see Table 4.5). Choose the highest-precedence group and use the longest continuous chain containing that functional group to establish the parent name and add the designated suffix for that group. Assign a number for its location, keeping this number as low as possible.

Second, name all other functional groups of lower precedence using the designated prefix, indicating their positions by numbers. If the compound containing a **double** or a **triple** bond, the **stem name** was modified from that of an alkane to that of an alkene or alkyne by inserting **-en-** or **-yn-** immediately before the highest-priority group's suffix.



4-hydroxycyclohex-2-enone



2-amino-3-pentynoic acid

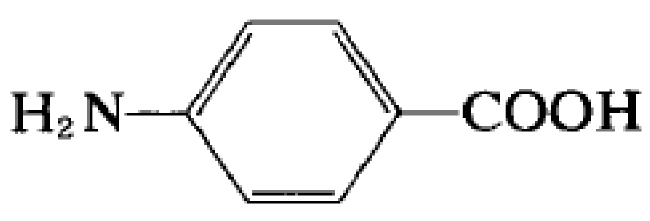
$H_2C{=}CHCH_2COCH_2CH_3$

hex-5-en-3-one

When the amino group is part of a compound containing an alcohol, carbonyl, or carboxylic acid functional group, it is named as a substituent.

$NH_2CH_2CH_2CH_2OH$

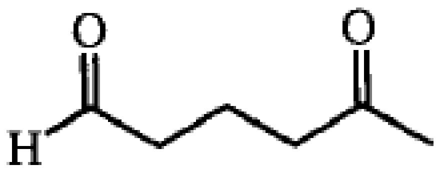
3-aminopropan-1-ol



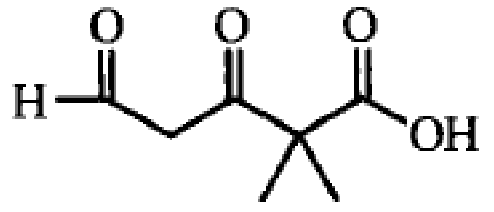
4-aminobenzoic acid

Here are some examples illustrating the application of these rules:

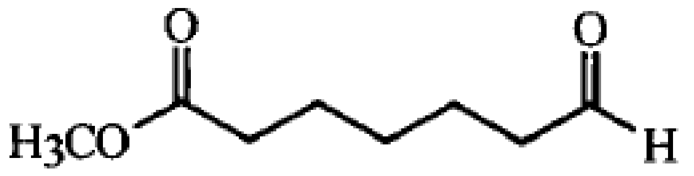
methyl-5-oxoheptanoate



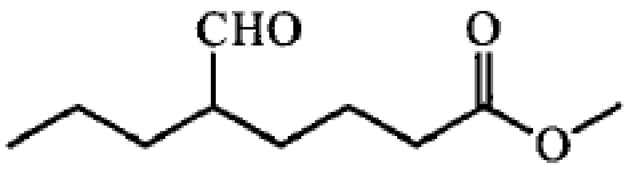
5-oxohexanal



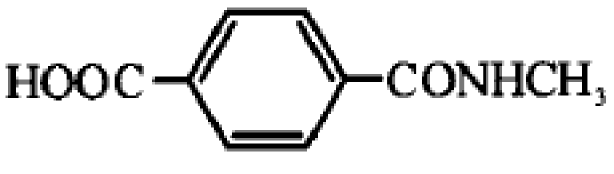
2,2-dimethyl-3,5-dioxopentanoic acid



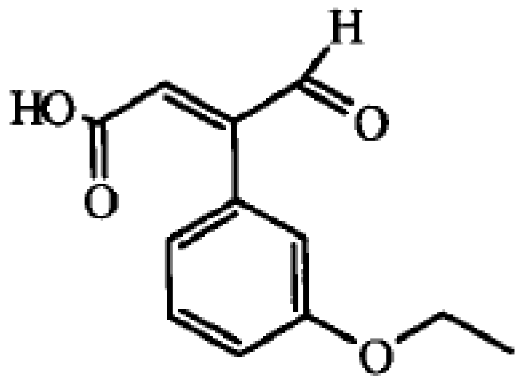
methyl-7-oxoheptanoate



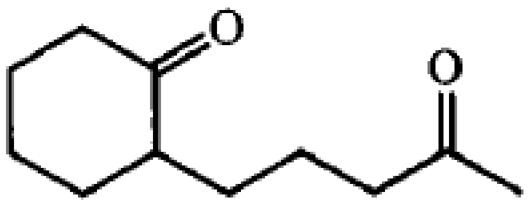
methyl-5-formyloctanoate



4-acetamidobenzoic acid



3-formyl-3-(3-ethoxyphenyl)-propenoic acid



2-(4-oxopentyl)cyclohexanone

$HOOC{-}CH_2OCH_2CH_2OCH_2{-}COOH$

2,2′-(ethylenedioxy)diacetic acid

$HOCH_2CH_2OCH_2CH_2OH$

2,2′-oxydiethanol

If a compound has two functional groups, the one with the lower priority is indicated by its prefix. The prefix of an aldehyde oxygen that is part of the parent hydrocarbon is "**oxo**". The prefix of a one-carbon aldehyde group that is not part of the parent hydrocarbon is "**formyl**".

References

[1] Panico R, Powell W H, Richer J C. A guide to IUPAC nomenclature of organic compounds: Recommendations [M]. London: Blackwell Scientific Publication, 1993.

[2] Moss G P, Smith P A S, Tavernier D. Glossary of class names of organic compounds and reactive intermediates based on structure [J]. Pure and Applied Chemistry, 1995 (67):1307-1376.

[3] Leigh Obe G J, Favre H A, Metanomski W V. Principles of chemical nomenclature: A guide to IUPAC recommendations [M]. London: Blackwell Science, 1998.

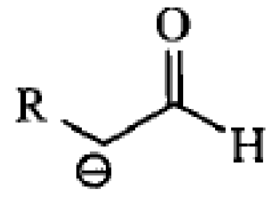
Chapter 5 Organic Chemistry

Organic chemistry is the chemistry of carbon-containing compounds. We study organic chemistry because just about every living organism, plant and animal, is composed of organic compounds, so the chemical reactions that take place in living systems, including our own bodies, are organic reactions. Many of synthetic compounds prevent shortages of naturally occurring products. Currently, there are about 16 million known organic compounds, and many more are possible. Anyone with an interest in life and living things needs to have a basic understanding of organic chemistry.

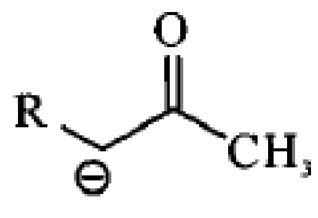
5.1 Nucleophiles and Electrophiles

Most organic reactions occur at the reactive sites of molecules and ions. These sites fall mainly into two categories.

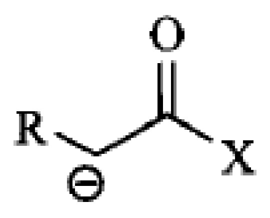
One category has a specific atom or region of the molecule which is electron rich. This is called the **nucleophilic center** and the species possessing such sites are called **nucleophiles** or electron-donors. The easiest nucleophiles to identify are negatively charged ions with lone pairs of electrons (e.g. the hydroxide ion). The nucleophilic center of a neutral molecule is usually an atom with a lone pair of electrons (e.g. nitrogen or oxygen) or a multiple bond (e.g. alkene, alkyne, aromatic ring). Examples of **nucleophiles** include those shown below:



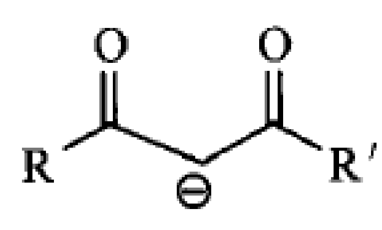
aldehyde



ketone



acid derivatives

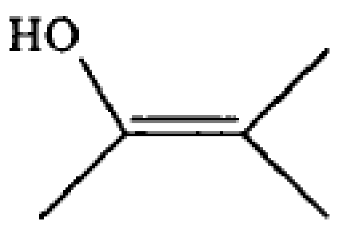


β-dicarbonyl compoupds

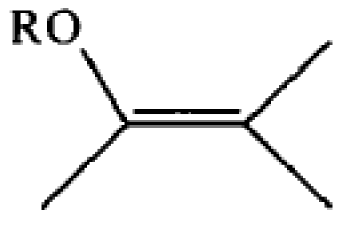
Organometallic compounds used as carbon nucleophiles include **Grignard reagents** (RMgX), organolithiums (RLi), organocuprates (R_2CuLi), and occasionally organocadmiums (R_2Cd) and organozincs (RZnBr).

Enolates including anionic derivatives of aldehydes, ketones, acid derivatives, and dicarbonyl compounds were used as carbon nucleophiles.

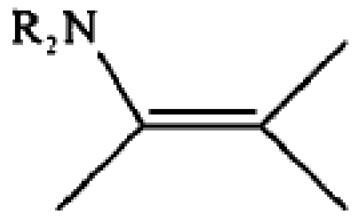
Enol derivatives of carbonyl compounds are covalent analogs of enolate ions. Enol derivatives are neutral derivatives of carbonyl compounds which have an oxygen or nitrogen substituent attached to a carbon-carbon double bond.



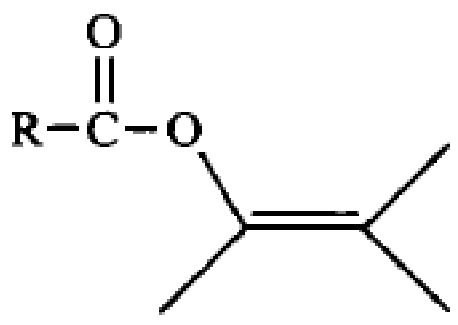
enol



enol ether



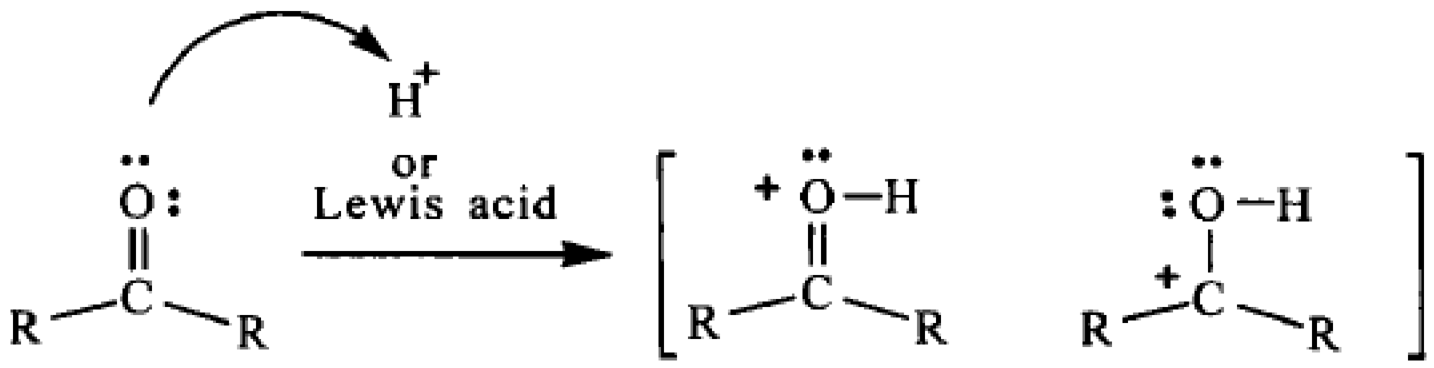
enamine



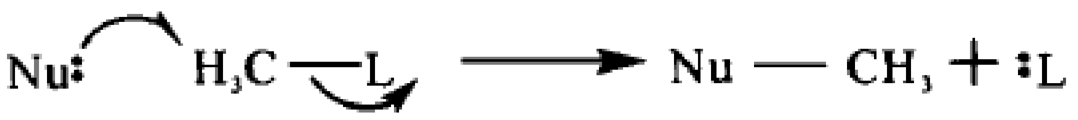
enol acetate

The second category has a specific atom or region of the molecule which is *electron —deficient* sites. This region is called the **electrophilic center**. Such electron-deficient sites are electrophilic and the species possessing such sites are called **electrophiles** or electron-acceptors. Positively charged ions can easily be identified as electrophiles (e.g. a carbocation). In a neutral molecule, the electrophilic center is an electron deficient atom within a functional group (e.g. a carbon or hydrogen atom linked to an electronegative atom such as oxygen, nitrogen, carbonyl groups and alkyl halides). Examples of **electrophiles** include those shown below.

Cationic carbon electrophiles are the most reactive because of the positive charge they carry. Compared to the carbonyl compound itself, the π^* orbitals of *oxonium* ions are much stronger electron acceptors.

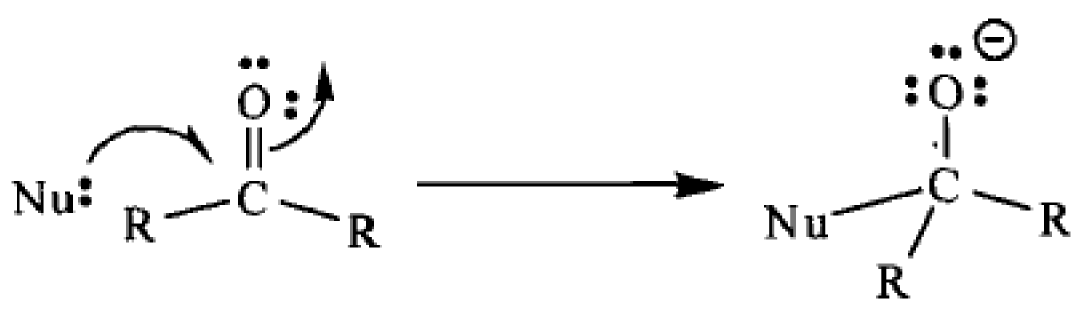


Aliphatic compounds with good leaving groups attached to primary or secondary carbon atoms are very commonly used as carbon electrophiles, such compounds include alkyl halides, alkyl sulfonates, and alkyl sulfates.

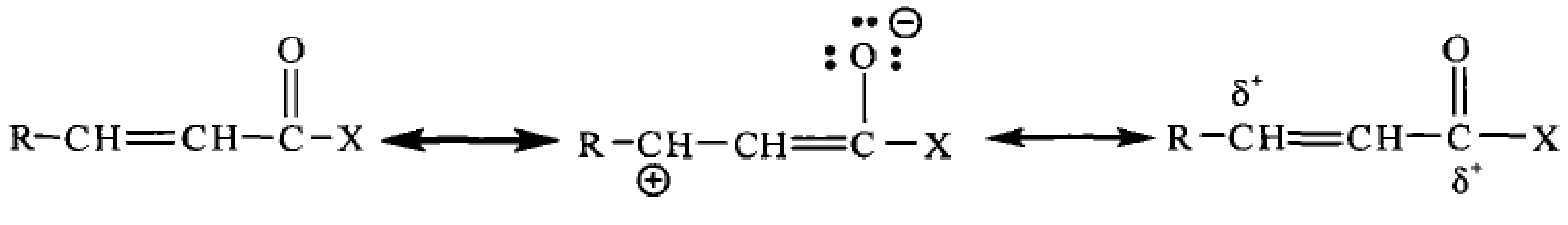


L= leaving group

Carbonyl compounds are very common carbon electrophiles by virtue of the polarized carbon-oxygen π bond.



α, β-Unsaturated carbonyl compounds can act as electrophiles under certain conditions and are bidentate in that both the carbonyl carbon and the β carbon are electron deficient. Thus nucleophiles can attack at either position.



5.2 Types of Reactive Intermediates

Many reactions occur by covalent bond formation between a nucleophilic and an electrophilic site. *Reactive intermediates* are short-lived species that are never present in high concentrations because they react as quickly as they are formed with a variety of compounds to give more stable products with tetravalent carbon atoms. Although reactive intermediates are not stable compounds, knowledge of the molecular and electronic structures of the most common organic intermediates are important to our study of organic chemistry. A mechanism simply involves an accounting of the formation and the destruction of the intermediates. Often the mechanism of a reaction is not considered complete until a detailed information about the nature and structure of the reactive intermediate is at hand. In most cases, reactive intermediates are fragments of molecules (like free radicals), often having atoms with unusual numbers of bonds. Some of the common reactive intermediates contain carbon atoms with only two or three bonds, compared with carbon's four bonds in its stable compounds. Common intermediates in organic reactions include **carbocations**, **radicals** (including **carbenes** and **radical ions**), and **carbanions** (Table 5.1). A great deal of meaningful synthetic and mechanistic work, in fact, is interpreted in terms of any one of the several different types of reactive intermediates.

Species with trivalent (three-bonded) carbon are classified according to their charge, which depends on the number of nonbonding electrons. The carbocations have no nonbonding electrons and are positively charged. The radicals have one nonbonding electron and are neutral. The carbanions have a pair of non bonding electrons and are negatively charged. The most common intermediates with a divalent (two-bonded) carbon atom are the carbenes. A carbene has two non bonding electrons on the divalent carbon atom, making it uncharged.

Table 5.1 Common intermediates

	Example	Name	Suffix
Radicals	$CH_3\cdot$	methyl	yl
	$CH_2:$	methylidene or carbene	ylidene or diyl
	$\cdot CH_2-CH_2\cdot$	ethane-1,2-diyl	
Anions	$CH_3-CH_2^-$	ethanide or ethyl anion	ide
Cations	CH_5^+	methanium	ium
	CH_3^+	methylium or methyl cation	ylium

5.2.1 Carbocations

A **carbocation** (also called a **carbonium ion** or a **carbenium ion**) is a species that contains a carbon atom bearing a positive charge. The positively charged carbon atom bears three substituents in a trigonal planar arrangement, and it has no nonbonding electrons. With only six electrons in the positive carbon's valence shell, the sp^2-hybridized atom is electron-deficient.

The stability of this intermediate is increased by substitution with alkyl substituents. An alkyl group stabilizes an electron-deficient carbocation in two ways: (1) through an **inductive effect**, and (2) through the **hyperconjugation**. In general, more highly substituted, carbocations are more stable, and the observed order of stability is tertiary > secondary > primary > methyl.

A carbocation (electron-deficient species) is a powerful electrophile (Lewis acid), and it may react with any nucleophile it encounters.

5.2.2 Radicals

Radicals are species (electron deficient) with at least one unpaired electron. A **free radical** containing an atom with an unpaired electron is highly reactive because it wants to acquire an electron to complete its octet. A radical contain a sp^2 hybridized carbon atom bearing three substituents in a trigonal planar arrangement. Unlike carbocations, however, the p orbital perpendicular to the trigonal plane of the there σ bonds of the radical is not empty; it contains the odd electron. Like carbocations, the stability of radicals is increased by the electron-donating effect of alkyl groups, more highly substituted radicals more stable. The observed order of stability is tertiary > secondary > primary > methyl. Free radical has no charge but may bear charges as in cationic- and anionic-radicals.

The **cation radical** can be formed by removal of an electron from the π bond of an alkene, resulting in the π system with unpaired-electron character (electron-deficient). The species can act as an electrophile.

Addition of an electron to an alkene produces an **anion radical** with two electrons in the π bonding orbital and the third electron must be placed in the π^* antibonding orbital.

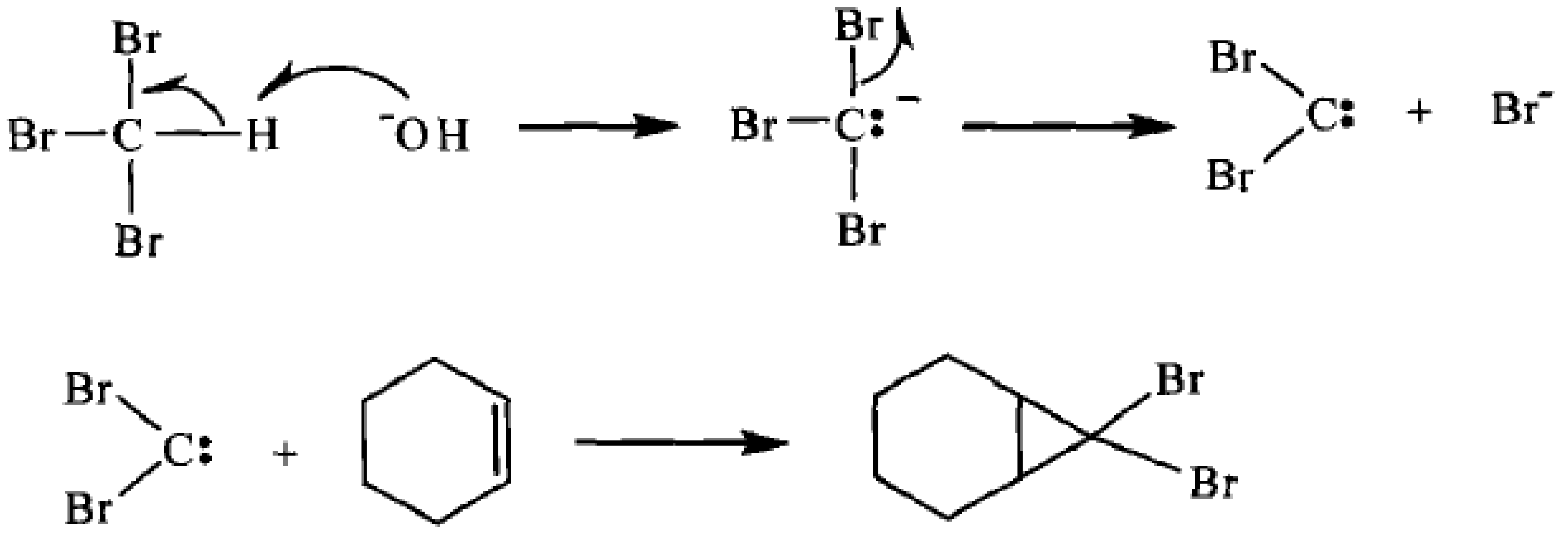
Carbenes are neutral species having a carbon atom with only two σ bonds and two electrons. There are two kinds: **singlet** in which the two electrons have opposite spins and are paired in one orbital, and **triplet** in which the two electrons have the same spin and are in different orbitals.

A singlet carbene is sp^2-hybridized. A p orbital is oriented perpendicular to the plane containing the two σ bonds and the additional sp^2-hybrid orbital. The electron pair is generally in the sp^2-hybrid orbital (rather than in the p orbital). This pair of electrons imparts nucleophilicity to a singlet carbene. On the other hand, there is a vacant p orbital that is an electrophilic center.

Triplet carbenes have two unpaired electrons, one in each of a sp^2 and a p orbital, while singlet carbenes have a pair of electrons in a nonbonding sp^2 orbital and have an empty p orbital.

The carbon atom in a carbene has only six electrons, therefore, it is an electron-deficient species analogous to a carbocation and normally reacts as a strong electrophile.

The most common synthetic reaction of carbenes is their addition to double bonds to form cyclopropane rings. For example, dibromocarbene adds to cyclohexene to give an interesting bicyclic compound.



5.2.3 Carbanions

A **carbanion** is pyramidal, rather than a planar geometry, with three sp^3 hybridized orbitals and the fourth hybrid orbital occupied by an unshared electron pair. A carbanion has the same electronic structure as an amine. Such a pyramidal structure undergoes inversion readily from one side of the plane to the other analogous to amines.

Carbanions are almost always bonded to stabilizing groups. They can be stabilized either by inductive effects or by resonance. For example, halogen atoms are *electron withdrawing*, so they stabilize carbanions through the inductive withdrawal of electron density. Resonance also plays an important role in stabilizing carbanions. A carbonyl group ($C=O$) stabilizes an adjacent carbanion by overlap of its π bond with the nonbonding electrons of the carbanion. The negative charge is delocalized onto the electronegative oxygen atom of the carbonyl group.

A carbanion has a negative charge on its carbon atom, making it a more powerful base and a stronger nucleophile than an amine.

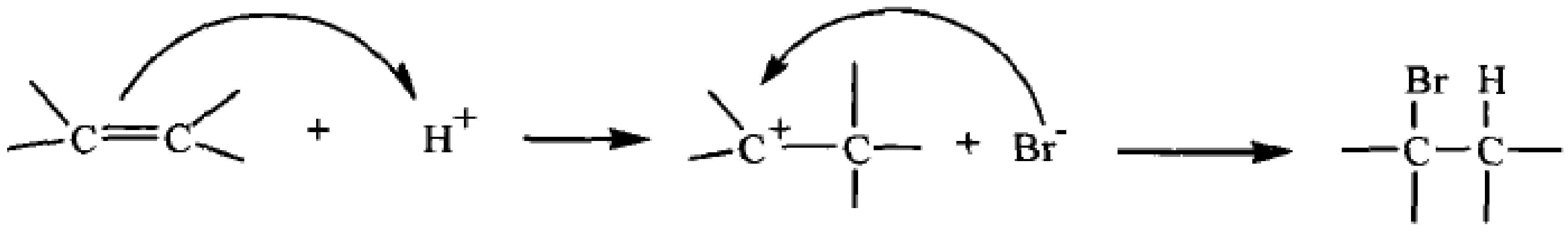
5.3 Classification of Reactions

In considering a new reaction, we first determine what is accomplished whether the number of atoms in the product differs from the number in the reactant, whether any atoms in the product are different from those in the reactant, and whether the positions of any atoms in the product differ from their positions in the reactant. Depending on the answers to these questions, we then classify a given chemical conversion as one of seven major organic reaction types: **addition**, **elimination**, **substitution**, **condensation**, **rearrangement**, **isomerization**, and **oxidation-reduction**.

5.3.1 Addition Reactions

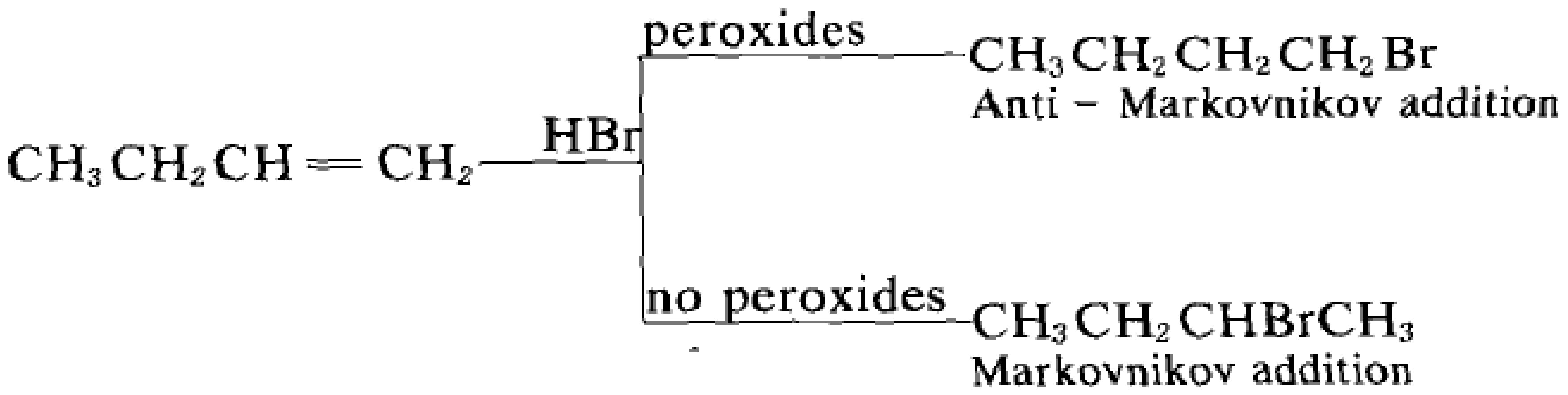
A reaction in which two reactant molecules combine to yield a single molecule of product containing the atoms of both reactants is called an **addition reaction**. Addition reactions are necessarily limited to compounds that contain atoms sharing more than one pair of electrons, that is, to compounds that contain multiply-bonded atoms. The reagent is simply added to the compound.

In the case of a proton reacting with π electrons of an alkene, the proton, an electrophilic (electron-loving) species, forms a bond with an alkene carbon atom. These reactions are called **electrophilic addition reactions.** After the proton reacts with the carbon atom, a **carbocation** is formed. A carbocation is an electron-deficient (**nucleus-loving**) carbon atom. A species with electrons to share (a Lewis base) can share its electrons with an electron-deficient species, such as the carbocation, this reaction is called a **nucleophilic addition reaction**.



electrophilic addition nucleophilic addition

One example of addition reactions is addition of hydrogen bromide of alkenes [**Markovnikov addition**: in electrophilic addition reactions a proton (the electrophile) will bond to the carbon atom in a double bond that already is bonded to the greater number of hydrogen atoms].



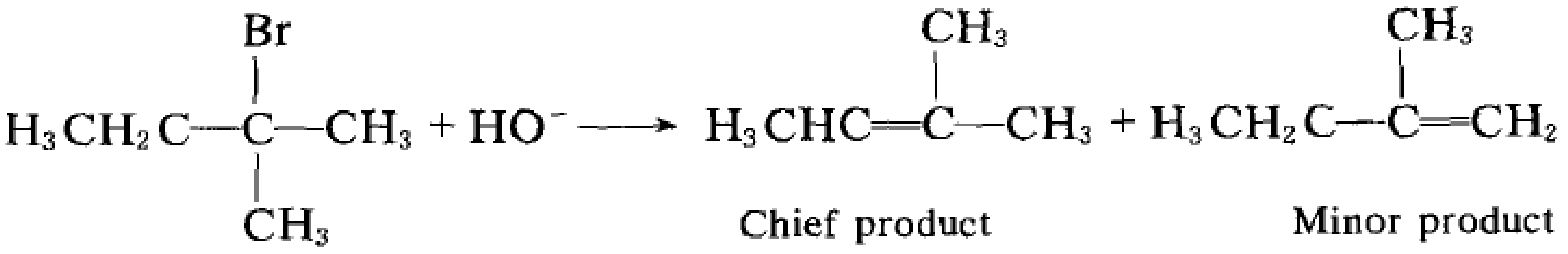
Diels-Alder (**D-A**) reactions represent a convenient way of making six-membered rings. This reaction is also called a (**4+2**) **cycloaddition reaction**.

5.3.2 Elimination Reactions

An **elimination reaction** is the opposite of an addition. In an elimination reaction, a single complex molecule splits into two simpler products: the one reactant molecule contains all the atoms present in two product molecules. If an elimination reaction removes two substituents from the same side of the C—C bond, the reaction is called a **syn elimination**. If the substituents are removed from opposite sides of the C—C bond, the reaction is called an **anti elimination**.

There are two important elimination reactions: **E1** and **E2**. "E" stands for elimination, "1" stands for unimolecular, and "2" stands for bimolecular. The product of an elimination reaction is an alkene. An E2 reaction is sometimes called a **β-elimination reaction**. It is also called a **1,2-elimination reaction**, because the atoms being removed are on adjacent carbons.

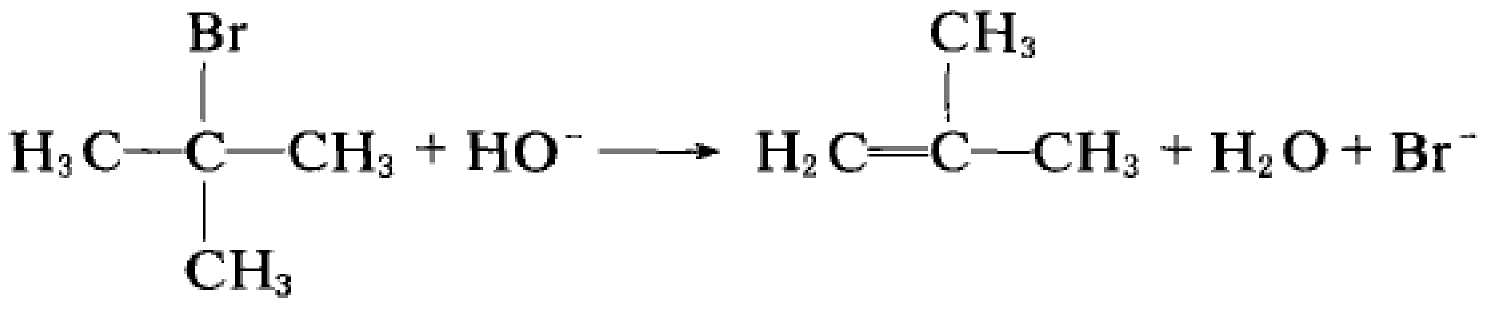
Removal of a proton and a halide ion is called **dehydrohalogenation**. When an alkyl halide undergoes an elimination reaction, the halogen (X) is removed from one carbon and a proton is removed from an adjacent carbon. A double bond is formed between the two carbons from which the atoms are eliminated (**Zaitsev's rule**: *the more substituted alkene product is obtained when a proton is removed from the β- carbon that is bonded to the fewest hydrogens*.)



$$H_3CH_2C\text{—}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}CH_3 + HO^- \longrightarrow H_3CHC{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{—}CH_3 + H_3CH_2C\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

Zaitsev's rule

The reaction of *tert*-butyl bromide with water to form 2-methylpropene is an example of an **E1 reaction**; the reaction of *tert*-butyl bromide with hydroxide ion is an example of an **E2 reaction**. Under these conditions, HBr is not observed directly, because, in the presence of base, it undergoes an acid-base reaction to form a salt.



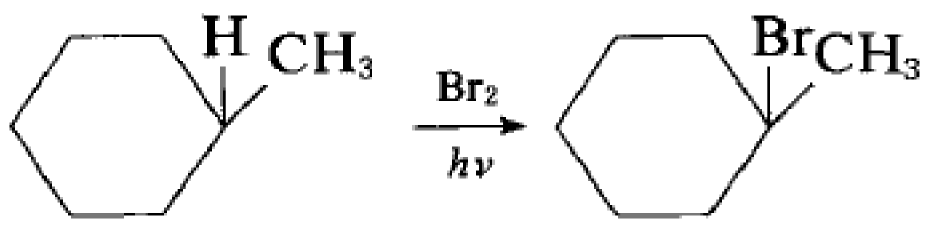
$$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}}-CH_3 + HO^- \longrightarrow H_2C=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 + H_2O + Br^-$$

The introduction of a carbon-carbon double bond into a molecule of all kinds must necessarily involve the elimination of atoms or groups from two adjacent carbons.

5.3.3 Substitution Reactions

In a **substitution reaction**, one atom or group of atoms in a molecule is replaced by another. For example, a hydrogen atom in methylcyclohexane is replaced by a bromine atom when the alkane is exposed to Br_2 in the presence of light or heat. In the products, the bromine is substituted at a position previously occupied by a hydrogen in methylcyclohexane, and hydrogen takes the place of one of the two bromine atoms in molecular bromine.

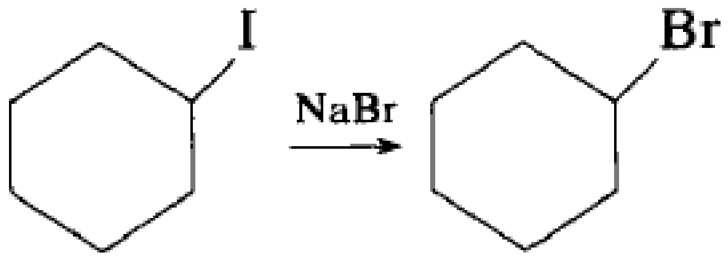
The reaction of an alkane with chlorine or bromine to form an alkyl halide is called a **radical substitution reaction** because radicals are involved as intermediates and the end result is the substitution of a halogen atom for one of the hydrogen atoms of the alkane. The substitution reaction is a **radical chain reaction** with **initiation**, **propagation**, and **termination steps**.



A variety of substitution reactions were studied and divided into two categories depending upon similar reaction characteristics. One category was given the name **SN2** reaction, where "**S**" stands for substitution, "**N**" stands for nucleophilic, and "**2**" stands for bimolecular. Bimolecular means that two molecules are involved in the rate-limiting step. Another series of substitution reactions carried out between nucleophiles and substrates has different characteristics from those of **SN2** reactions. This type of reaction is called **SN1** reaction, where "1" stands for unimolecular. Unimolecular means that only one molecule is involved in the rate-determining step. Unlike an **SN2** reaction, where the leaving group departs and the nucleophile approaches *at the same time*, the leaving group in an SN1 reaction departs *before* the nucleophile approaches.

Alkyl halides undergo two kinds of **nucleophilic substitution reactions**: **SN2** and **SN1**. In both reactions, a nucleophile substitutes for a halogen, which is called a **leaving group**. **SN1** reactions occur with 3° and 2° alkyl halides. **SN2** reactions occur with methyl halides and 1° and 2° alkyl halides.

For example, the treatment of cyclohexyl iodide with sodium bromide in acetone solvent is a substitution reaction. The electronegative iodine is replaced by bromine in the products. When one electronegative group is substituted for another, no change in oxidation level occurs; thus the reagents which carry out such substitutions are neither oxidants nor reductants.



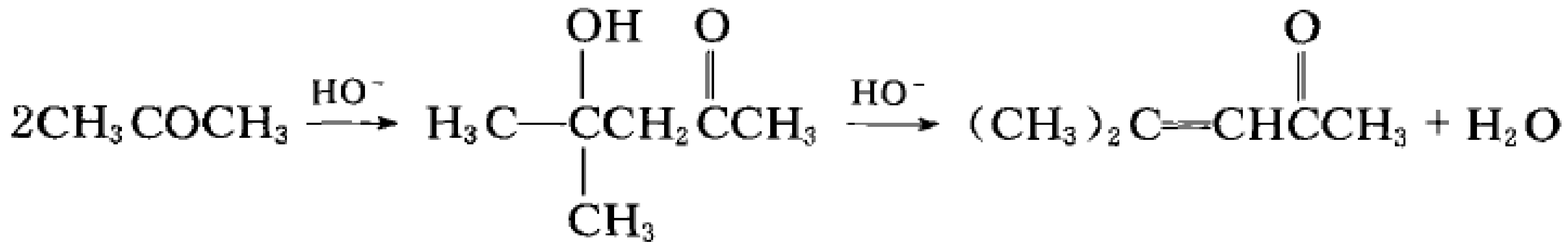
As far as the aromatic ring is concerned, **Friedel-Crafts alkylation** and **Friedel-Crafts acylation** reactions represent convenient **electrophilic substitution reactions**.

5.3.4 Condensation Reactions

A **condensation reaction** is a reaction that combines two molecules to form a more complex product while removing a small molecule (usually water or an alcohol).

For example, the combination of a carboxylic acid with an alcohol in the presence of an acid catalyst produces an ester (a more complex molecule) and water (a small molecule). In this reaction, two different organic reactants (an acid and an alcohol) combine to form an ester. The product ester has fewer atoms than the sum of those in the two reactants because water is formed as a by-product.

The **aldol condensation** reaction is an example of a condensation reaction in which a carbon-carbon bond is formed. In the aldol condensation, a carbanion generated (as a nucleophile) from one molecule of ketone or aldehyde adds to the carbonyl group of a second molecule, forming β-hydroxyketone or β-hydroxyaldehyde. The β-hydroxyketone can also be dehydrated under basic conditions, so heating the aldol addition product in either acid or base leads to dehydration. The product of dehydration is called an **enone**—"**ene**" for the **double bond** and "**one**" for the **carbonyl group**.



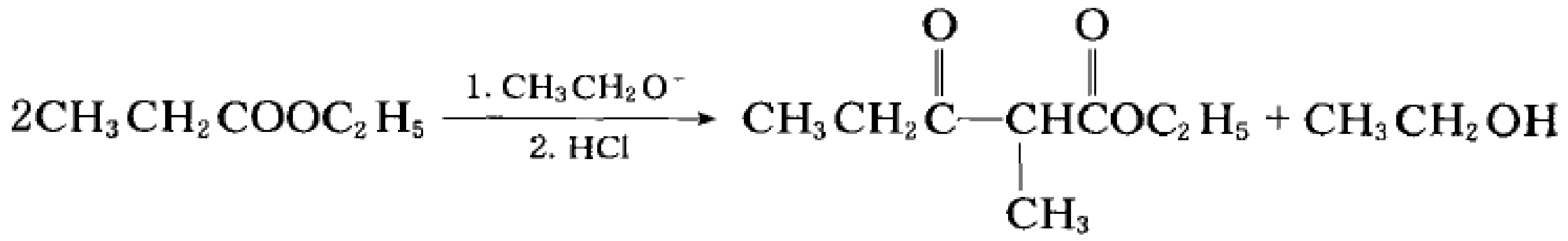
$$2\mathrm{CH_3COCH_3} \xrightarrow{\mathrm{HO^-}} \mathrm{H_3C}-\overset{\overset{\mathrm{OH}}{|}}{\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\mathrm{CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3} \xrightarrow{\mathrm{HO^-}} \mathrm{(CH_3)_2C{=}CH}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3} + \mathrm{H_2O}$$

β-hydroxyketone

enone
α,β-unsaturated ketone

There are a large number of condensations that are closely related to the aldol condensation. Each of these reactions has its own name, for example, **Perkin**, **Knoevenagel**, **Claisen** and **Dieckmann**. Each of these involves attack by a carbanion on a carbonyl group like the aldol condensation. In each case the carbanion is generated in very much the same way: the abstraction by base of a hydrogen ion alpha to a carbonyl group.

When two molecules of an *ester* undergo a condensation reaction, the reaction is called a **Claisen condensation**. The product of a Claisen condensation is an ester with acyl substitution (β-keto ester). A **Dieckmann condensation** is an intramolecular Claisen condensation.



$$2\mathrm{CH_3CH_2COOC_2H_5} \xrightarrow[\mathrm{2.\ HCl}]{\mathrm{1.\ CH_3CH_2O^-}} \mathrm{CH_3CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OC_2H_5} + \mathrm{CH_3CH_2OH}$$

β- keto ester

The **Perkin condensation** is the condensation of an aromatic aldehyde and acetic anhydride.

$$\mathrm{C_6H_5CHO} + \mathrm{(CH_3CO)_2O} \xrightarrow{\mathrm{CH_3COONa}} \mathrm{C_6H_5CH{=}CHCOOH}$$

The **Knoevenagel condensation** is the condensation of an aldehyde or unhindered ketone and a saturated α,β-dicarbonyl compound such as diethyl malonate that has two electron-withdrawing groups, forming α, β-unsaturated carbonyl compounds.

$$C_6H_5CHO + CH_2(COOC_2H_2)_2 \xrightarrow{2^{\circ}\ \text{amine}} C_6H_5CH{=}C(COOC_2H_5)_2$$

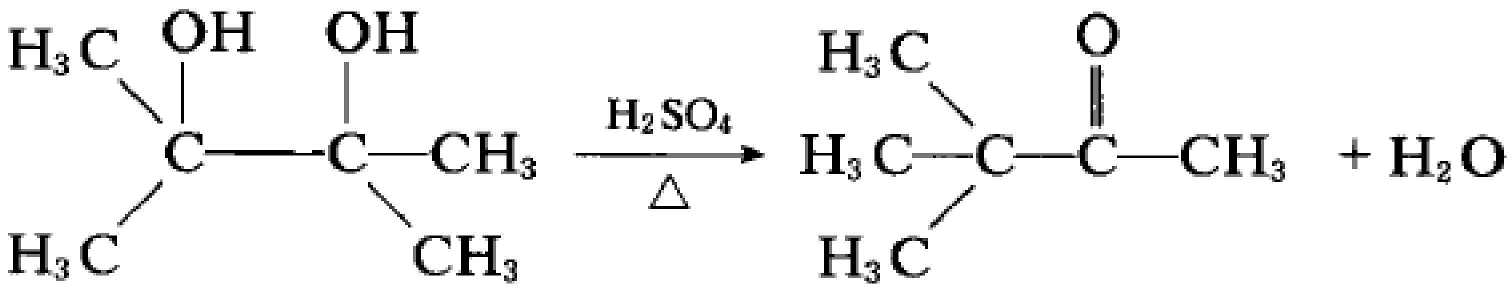
5.3.5 Rearrangement Reactions

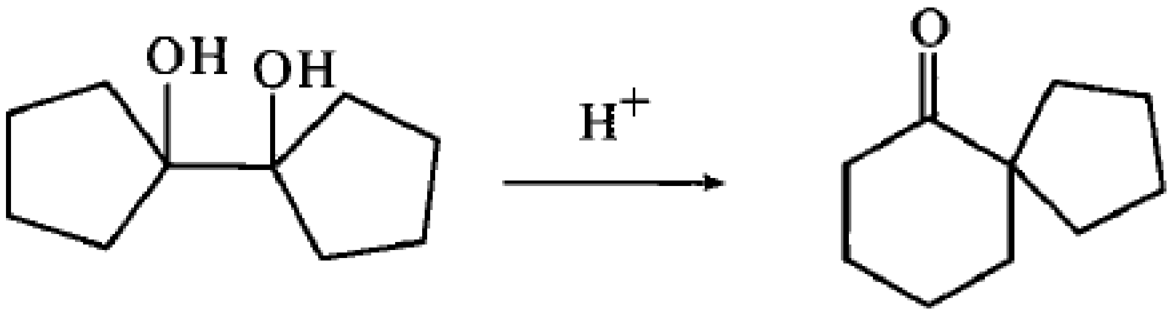
Rearrangement reactions occur when one starting material forms one product with a different arrangement of atoms and bonds.

There are a large number of rearrangements. Each of these reactions has its own name, for example, **Beckmann**, **Pinacol**, **Claisen**, **Curtius**, **Favorskii**, **Baeyer-Villiger**, **Cope** and **Hofmann rearrangement**.

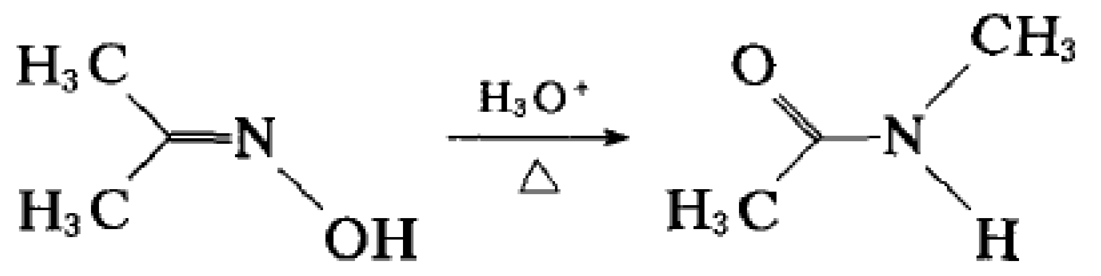
In a rearrangement reaction, the atoms or groups present in the reactant are connected in a different fashion in the product. The reactant and the product can have the same empirical formula, as in the Beckmann rearrangement, or different numbers and types of atoms, as in the pinacol rearrangement, in which water is formed as a by-product.

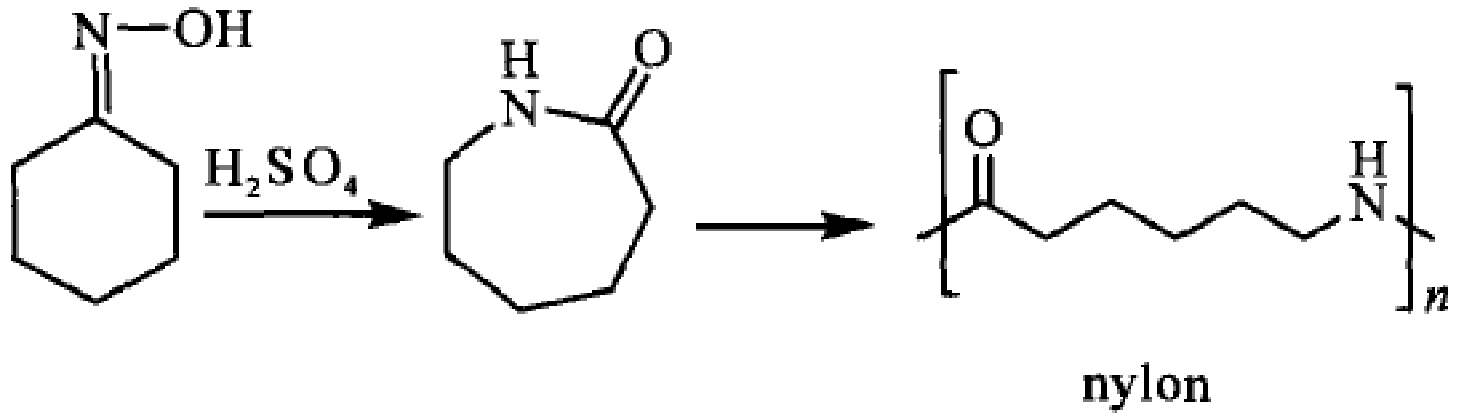
A vicinal diol "**pinacol**" has —OH groups on adjacent carbons. The dehydration of a vicinal diol is accompanied by a rearrangement called the **pinacol rearrangement**. In the pinacol rearrangement, a methyl group migrates from one carbon to the adjacent carbon, a C=O bond appears in the product, and a molecule of water is lost from the reactant.



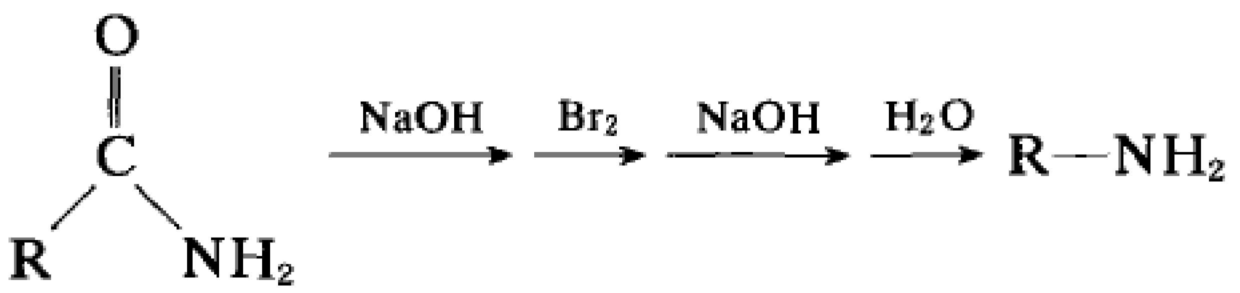


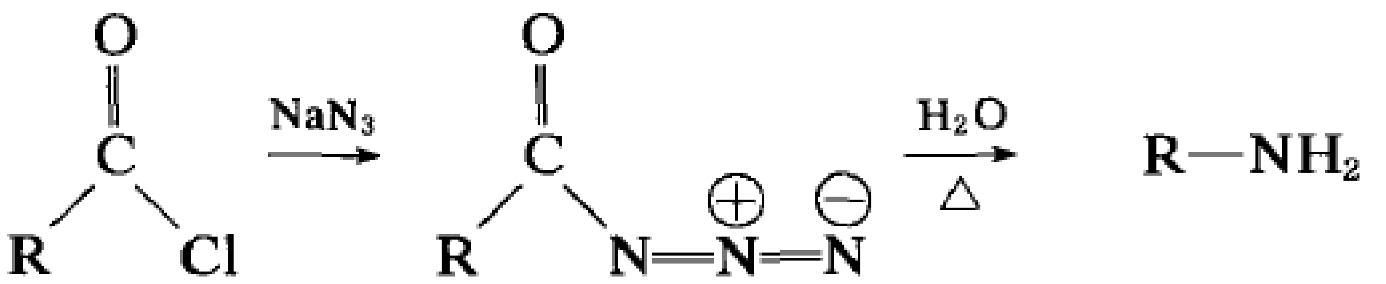
In the **Beckmann rearrangement**, an alkyl group originally attached to carbon becomes attached to nitrogen, a N—O bond in the reactant is broken, and a C=O bond appears in the product. The industrial manufacture of nylon relies upon the Beckmann rearrangement: the alkaline polymerization of a cyclic amide produced by the action of sulfuric acid on the oxime of cyclohexanone.



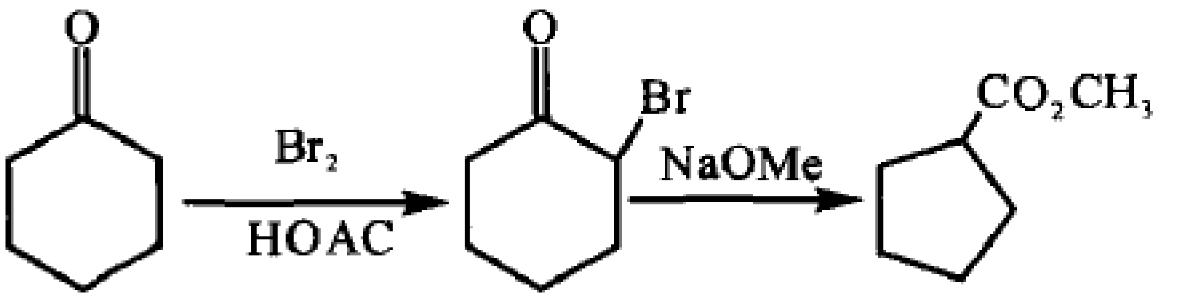


In the **Hofmann rearrangement** an amide turns into an amine with loss of a carbon atom. In the **Curtius rearrangement** an acid chloride converts to an amine with loss of a carbon atom. In both cases the rearrangement reaction involves the alkyl group being transferred from the carbonyl group to the nitrogen atom to form an isocyanate intermediate. Hydrolysis then results in loss of the original carbonyl group. The Hofmann rearrangement involves the treatment of a primary amide with bromine under basic conditions. The Curtius rearrangement involves heating an acyl azide.

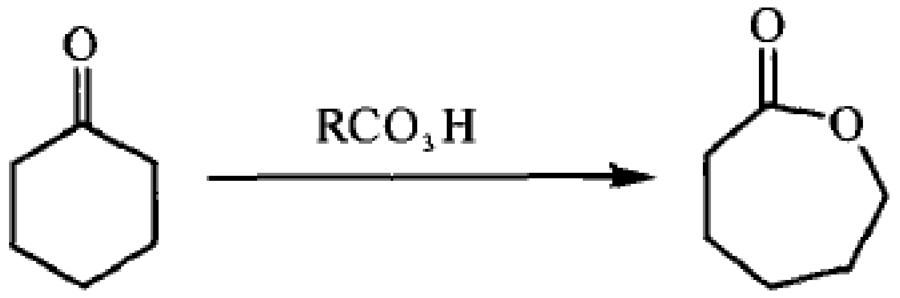




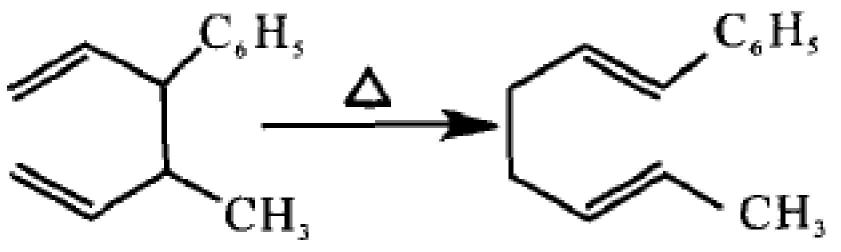
The **Favorskii rearrangement** turns an α-halo ketone to an ester. Favorskii rearrangement of cyclic 2-bromoketones leads to ring contraction and this has become one of the most fruitful uses of the rearrangement in synthesis.



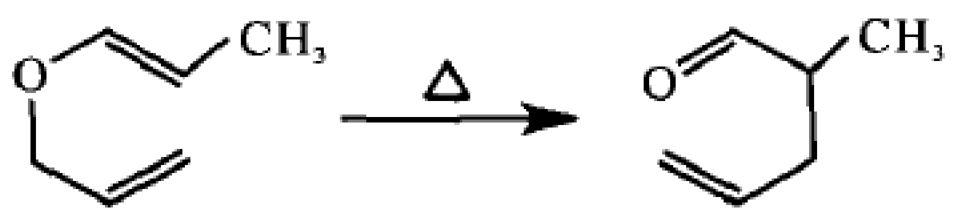
In the **Baeyer-Villiger rearrangement reaction**, treating a ketone with a peroxy-acid (RCO_3H) can produce an ester. An oxygen atom is "inserted" next to the carbonyl group.



The **Cope rearrangement** is a [3,3] sigmatropic rearrangement of a 1,5-diene. The **Claisen rearrangement** is a [3,3] sigmatropic rearrangement of an allyl vinyl ether. Both rearrangements form six-membered-ring transition states.

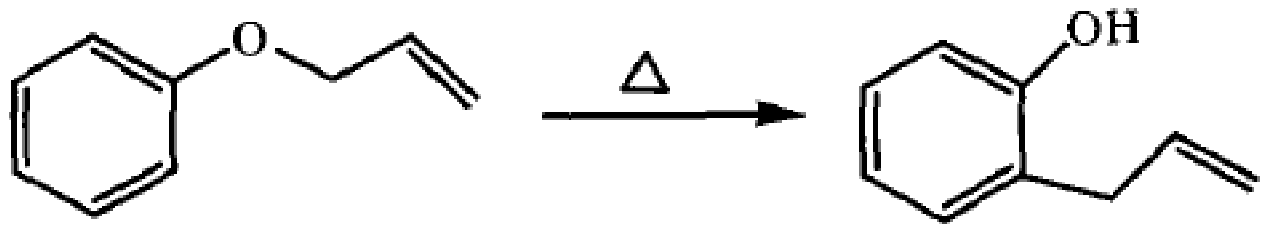


Cope rearrangement



Claisen rearrangement

The **Claisen rearrangement** reaction is a useful method of obtaining *ortho*-alkyl phenols since the double bond can be subsequently hydrogenated. On heating, an allyl phenyl ether undergoes a concerted rearrangement reaction which results in the allyl group being transferred from the phenol group to the *ortho* carbon.



5.3.6 Oxidation-reduction Reactions

Oxidation and reduction of organic molecules are important processes and have played an extremely important role in organic synthesis.

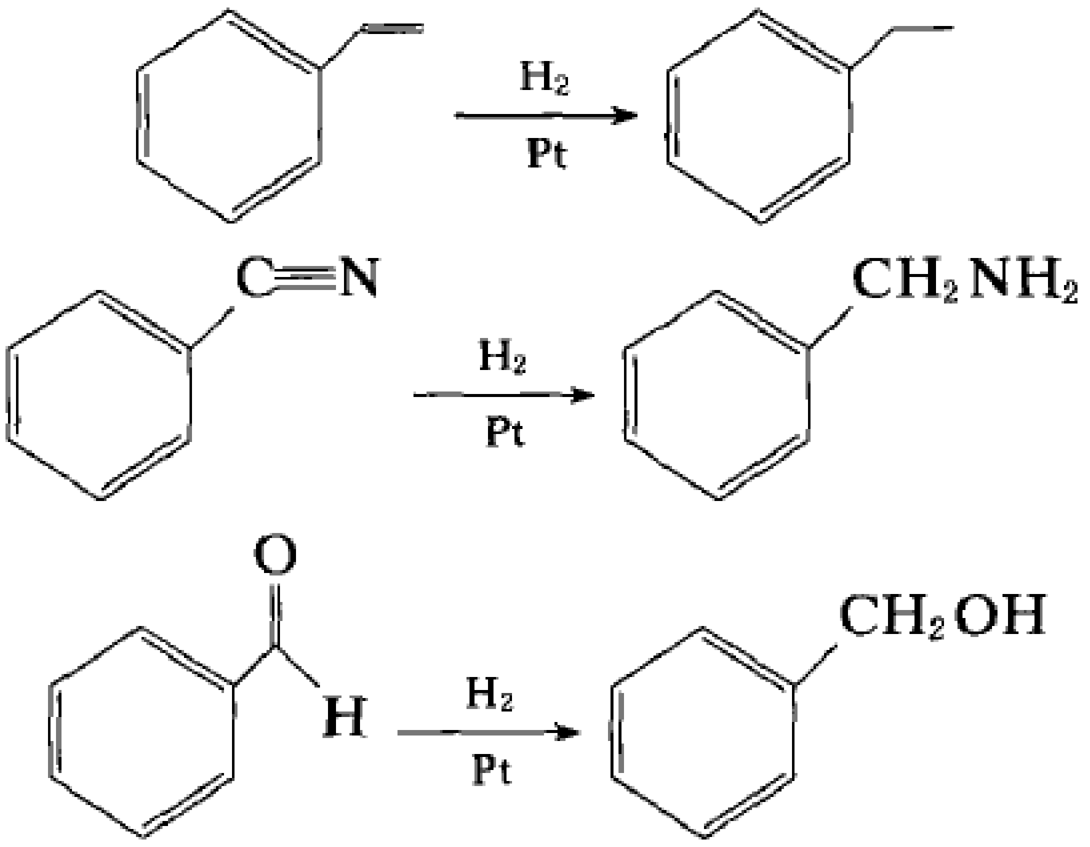
The term oxidation in organic chemistry differs from that in inorganic chemistry. *Oxidation in organic chemistry usually implies removal of hydrogen or replacement of a hydrogen atom linked to carbon with a more electronegative atom such as oxygen.*

It is easy to tell whether an organic compound has been oxidized or reduced simply by looking at the change on carbon atoms in the structure of the compound: if the reaction increases the number of C—H bonds or decreases the number of C—O, C—N, or C—X bonds (where X denotes a halogen), the compound has been reduced. if the reaction decreases the number of

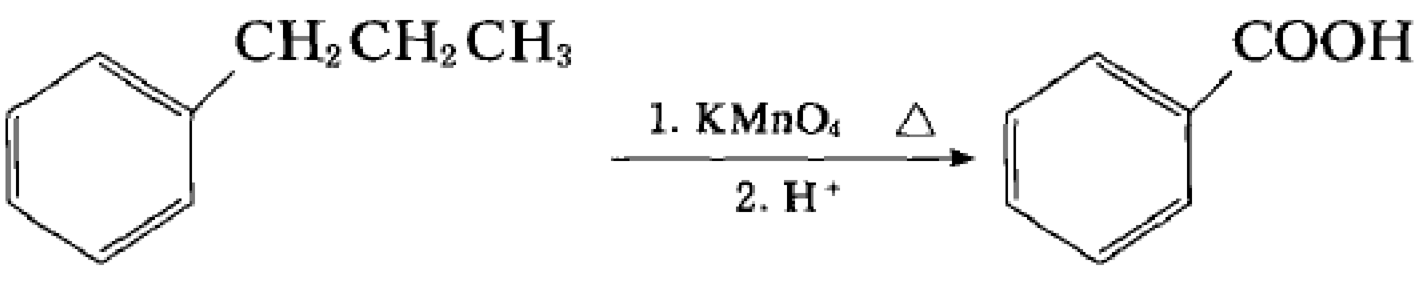
C—H bonds or increases the number of C—O, C—N, or C—X bonds, the compound has been oxidized. Notice that the oxidation state of a carbon atom equals the total number of its C—O, C—N or C—X bonds.

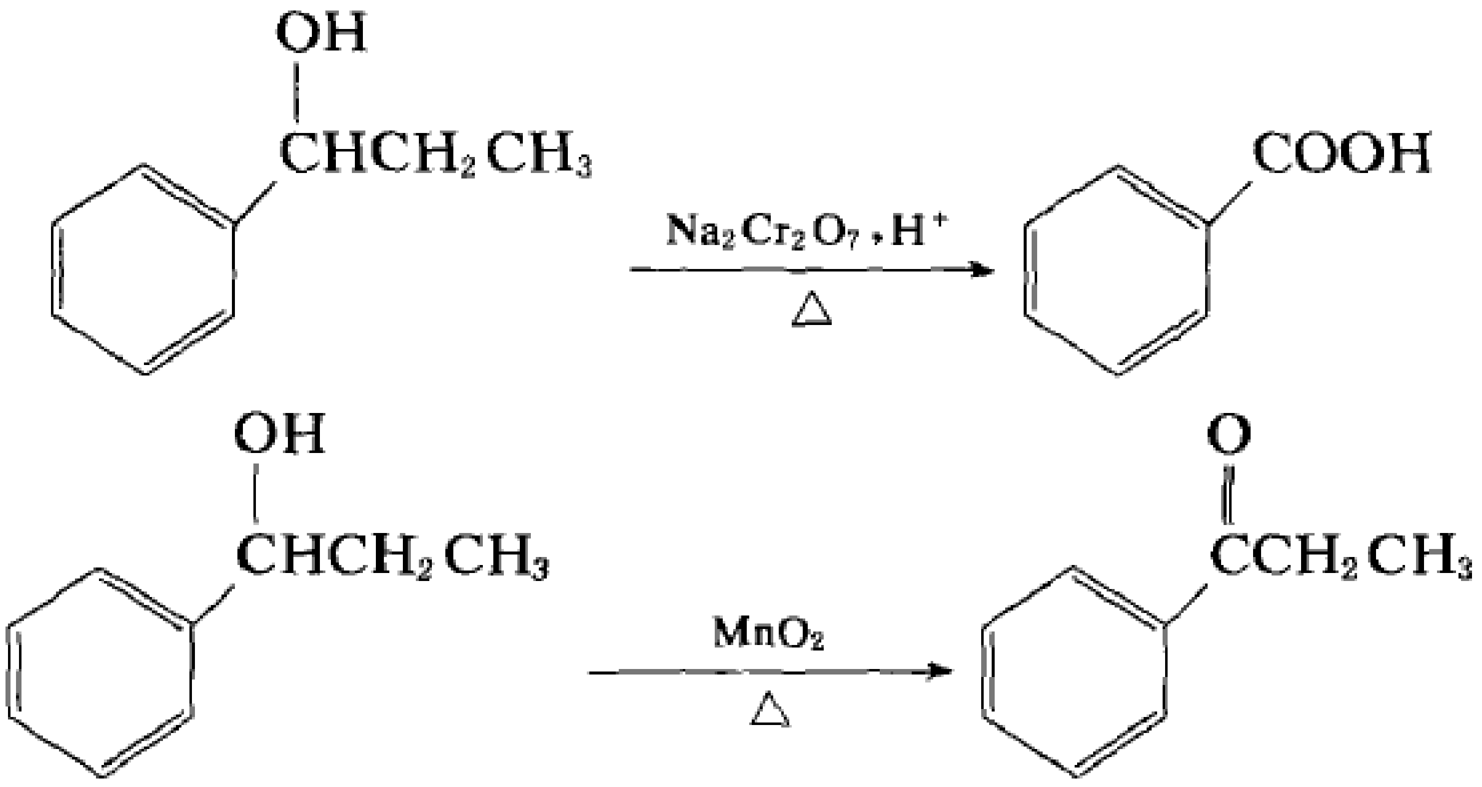
In oxidation-reduction reactions, there is a net formal change in oxidation level of one or more carbon atoms in a molecule. These reactions can often also be classified as substitutions (when the number of heteroatoms at a given carbon is changed), additions (when hydrogen is added across a multiple bond), or eliminations (when the elements of molecular hydrogen have formally been removed from adjacent atoms). Oxidation-reduction reactions are referred to as redox reactions, to emphasize the need to use oxidizing or reducing reagents to bring them about.

Substituents with double and triple bonds can undergo catalytic hydrogenation in the presence of excess hydrogen and a suitable metallic catalyst such as Pt, Ni, Pd, Ru, etc., which are the most common currently employed metals. The hydrogen molecule adds across a double or triple bond.



Benzene is an unusually stable compound, it will not be oxidized, but an alkyl group bonded to a benzene ring can be oxidized to a carboxyl group. Regardless of the length of the alkyl substituent, it will be oxidized to a COOH group, provided that a hydrogen is bonded to the benzylic carbon. Commonly used oxidizing agents are potassium permanganate or acidic solutions of sodium dichromate.

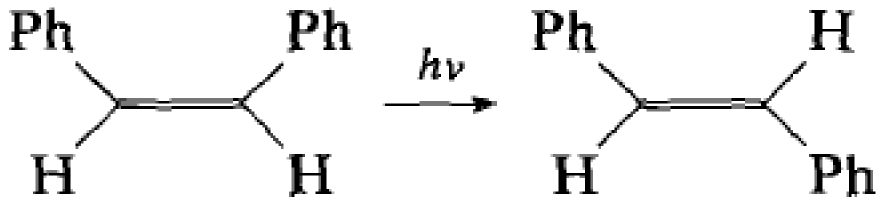




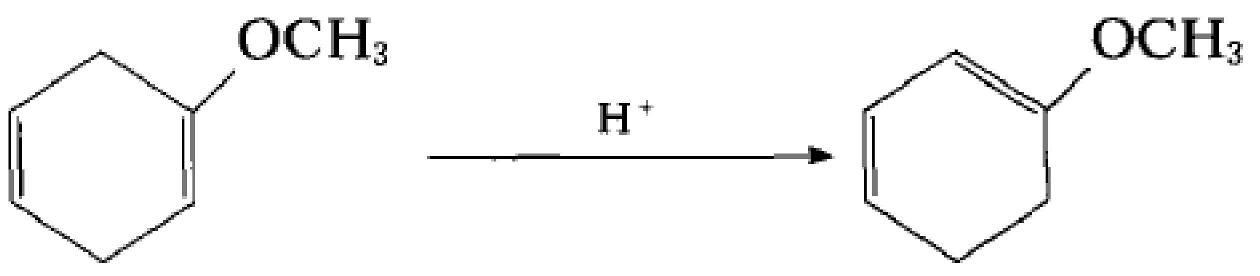
5.3.7 Isomerization Reactions

An **isomerization** is a reaction in which species with the same molecular formula, but different structures, are interconverted. In a rearrangement, the carbon skeleton can be the same (as in the Beckmann rearrangement) or different (as in the pinacol rearrangement). *An isomerization differs from a rearrangement in that the carbon skeleton remains intact, but the disposition of substituents or functional groups in space is changed.*

There are two types of isomerization reactions: **geometric and positional**. In a geometric isomerization, all atoms in the product are attached to the same atoms as in the reactant, but the disposition in space of the bonds connecting them is changed. In a positional isomerization, the position (or positions) of one or more substituents or functional groups in the product differs from the original position(s) in the reactant. For example, the conversion of (*Z*)-1,2-diphenylethene to (*E*)-1,2-diphenylethene is a geometric isomerization, and that of 1-methoxycyclohexa-1,4-diene to 1-methoxycyclohexa-1,3-diene is a positional isomerization. Geometric isomers differ only in the position of atoms or groups in space (*Z*-and *E*-1,2-diphenylethene); positional isomers differ in the position of a functional group in the molecule (1-methoxycyclohexa-1,4-diene and 1-methoxycyclohexa-1,3-diene).



(*Z*)-1,2-diphenylethene (*E*)-1,2-diphenylethene



1-methoxycyclohexa-1,4-diene 1-methoxycyclohexa-1,3-diene

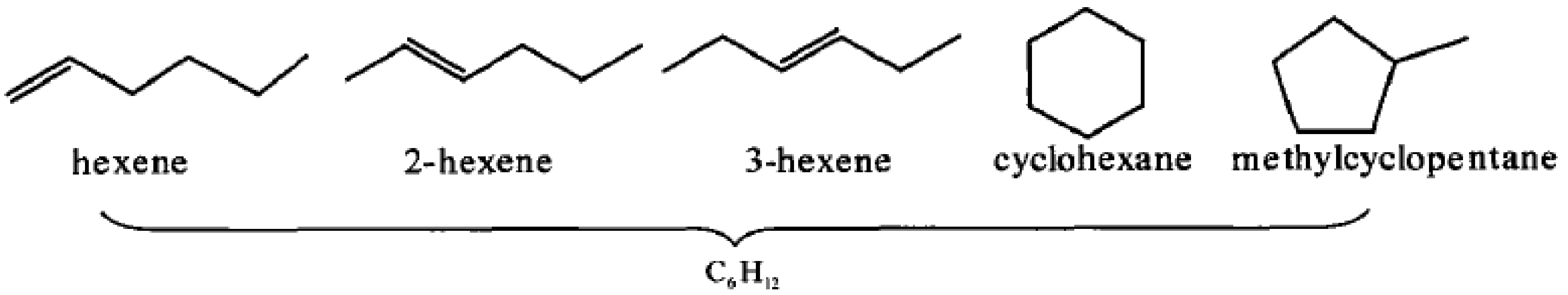
5.4 Stereochemistry

Stereochemistry is the study of the three-dimensional structure of molecules. No one can understand organic chemistry, biochemistry, or biology without using stereochemistry. Differences in spatial orientation might seem unimportant, but stereoisomers often have remarkably different physical chemical and biological properties. For example, butenedioic acid ($\mathrm{HOOC{-}CH{=}CH{-}COOH}$) has a ***cis*** and a ***trans*** isomers. The *trans* isomer (fumaric acid) is an essential metabolic intermediate in both plants and animals, but the *cis* isomer (maleic acid) is toxic and irritating to tissues.

Isomers are compounds which have the same molecular formula, but differ in the way the atoms are arranged. There are three types of isomers: **constitutional**, **configurational**, and **conformational** (Figure 5.1).

5.4.1 Constitutional Isomers

Constitutional isomers (structural isomers) are compounds with the same molecular formula, but their atoms are connected differently. Constitutional isomers have different physical and chemical properties. Alkanes of a particular molecular formula can have various constitutional isomers. The larger the alkane, the more isomers which are possible.



hexene 2-hexene 3-hexene cyclohexane methylcyclopentane

C_6H_{12}

5.4.2 Configurational Isomers

Configurational isomers have the same molecular formula and the same

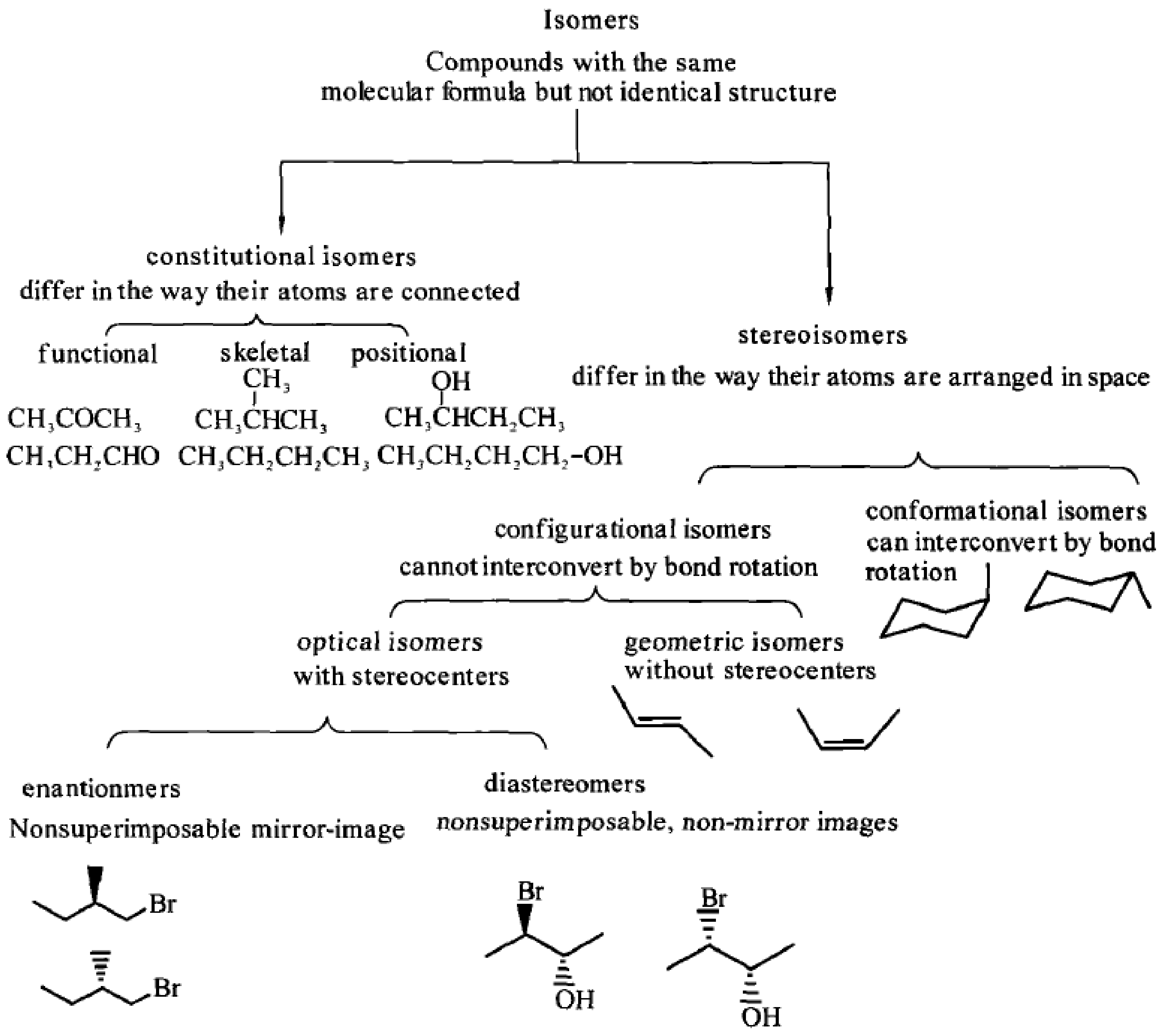
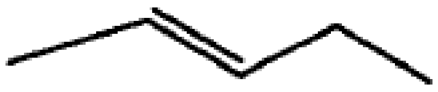


Figure 5.1 Isomerism in organic chemistry.

bonds. However, some of the atoms are arranged differently in space with respect to each other, and the isomers cannot be interconverted without breaking a covalent bond. Substituted alkenes and cycloalkanes can exist as configurational isomers.

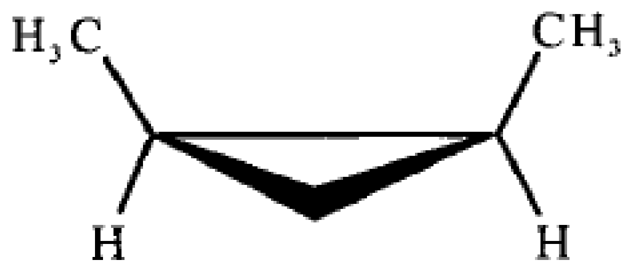
Alkenes having two different substituents at each end of the double bond can exist as two configurational isomers. The ***cis*** and the ***trans*** nomenclature for alkenes is an old method of classifying the configurational isomers of alkenes. Simple alkenes can be defined as *cis* or *trans* depending on whether substituents at different ends of the alkene are on the same side of the alkene (i.e. *cis*) or on opposite sides (i.e. *trans*).

cis-pent-2-ene

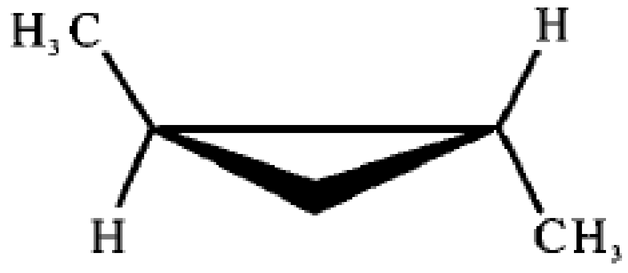


trans-pent-2-ene

Substituted cycloalkanes can exist as configurational isomers where the substituents are *cis* or *trans* with respect to each other.



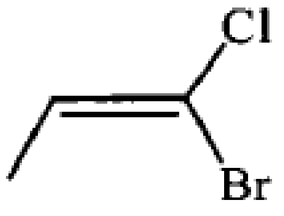
cis-1,2-dimethylcyclopropane



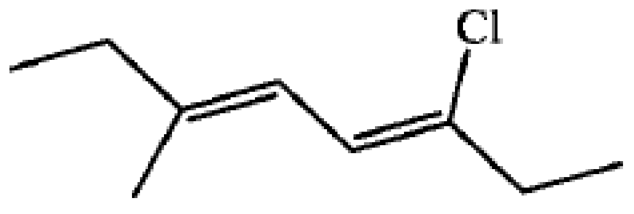
trans-1,2-dimethylcyclopropane

Alkenes can be assigned as ***Z*** or ***E*** depending on the relative positions of priority groups. Priority groups are determined by the atomic numbers of the atoms directly attached to the alkene. If there is no distinction between these atoms, the next atom of each substituent is compared. If the priority groups at each end of the alkene are on the same side of the double bond, the alkene is designated as **Z** (from the German word "*zusammen*" meaning *together*). If they are on opposite sides, the alkene is defined as ***E*** (from the German word "*entgegen*" meaning *across*).

(*E*)-1-bromo-1-chloroprop-1-ene



(*Z*)-1-bromo-1-chloroprop-1-ene



3-chloro-6-methyl-(3*Z*,5*E*)-octa-3,5-diene

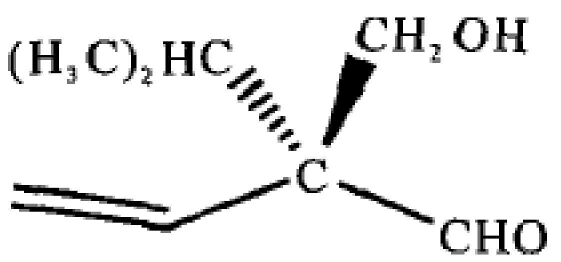
Compounds which are not identical with their mirror images are said to be **chiral**, while compounds which are identical with their mirror images are said to be **achiral**. **Chirality** is a property of two configurational isomers which are nonidentical mirror images. **Optical isomers** are configurational isomers which have the ability to rotate plane-polarized light clockwise or counter-clockwise. The term was loosely applied to more than one type of isomerism among optically active compounds, and this ambiguous term has been replaced by the well-defined term **enantiomers**.

Whenever a molecule has two or more asymmetric centers, there are several possible structures which are possible and we need to use terms such as **stereoisomers**, **diastereomers** and **enantiomers** to discuss them.

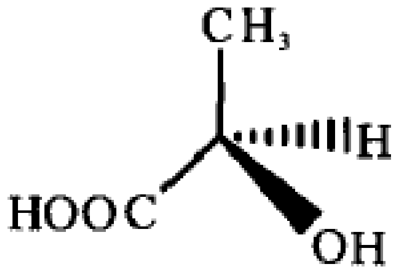
The most important type of **stereoisomerism** is that which arises when molecules possess two structures that are not identical and also are mirror images of one another. Such molecules can also be termed as **chiral molecules** and as such can exist as two nonsuperimposable mirror images. These mirror images are **optical isomers** and are a form of **configurational isomerism**. Pairs of nonsuperimposable mirror-image molecules are called **enantiomers**. The observation of optical activity and the measurement of optical rotation distinguish one enantiomer (+) from the other (−). The symbols (+) and (−) are used to show which direction an enantiomer rotates plane-polarized light. The direction of rotation can only be determined by experimentation.

A second way to designate these stereoisomers is to assign the configurations as **R** or **S** based on stereostructures (for enantiomers which contain a single chiral center). The R and S configurations are relative configurations based on three-dimensional structures which are drawn on paper. However, it is not possible to predict a priori whether the **R enantiomer** (for example) will be **dextrorotatory** (+) or **levorotatory** (−).

The structure of an enantiomer can be specified by the R and S nomenclature determined by the **Cahn-Ingold-Prelog** rules. The groups attached to the chiral center are given priorities based on the atomic weights of the atoms directly attached to the center. If there is no distinction between these atoms, the next atom of each substituent is compared. The group of lowest priority is oriented directly away from your eye. If the direction of the remaining groups from the highest to lowest priority is **clockwise**, the configuration is designated **R**; if the procession is **counterclockwise**, the configuration is designated **S**. The assignment of an asymmetric center as R or S has nothing to do with whichever direction the molecule rotates plane-polarized light. Optical rotation can only be determined experimentally.



(*S*)-2-(hydroxymethyl)-2-isopropylbut-3-enal

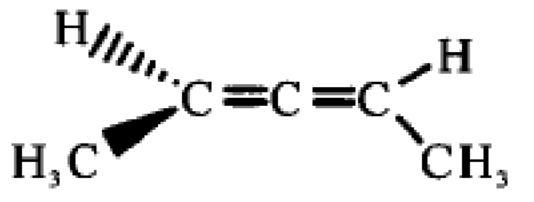


R-(−)-lactic acid
(*R*)-2-hydroxypropanoic acid

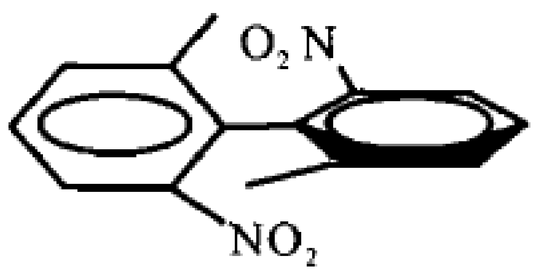
Optical purity is quoted in terms of **enantiomeric excess**. This indicates the excess of pure enantiomer over racemate. The composition of the mixture is denoted by the optical purity or the **percent enantiomeric excess** (**ee %**). The enantiomeric excess is defined as **ee % = major enantiomer% − minor enantiomer%** and is a measure of the optical purity of the sample.

The **diastereoselectivity** for any process is often reported as a **diastereomeric excess** (**de %**), which is analogous to the optical purity reported for mixtures of enantiomers. The de % is given by **de %= major diastereomer% − minor diastereomer%**.

Some substituted allenes, biphenyls and spiro compounds are chiral molecules despite the lack of a chiral center. The molecular chirality arises from the presence of a screw axis in the molecule. Because they are chiral, they exist as enantiomers.

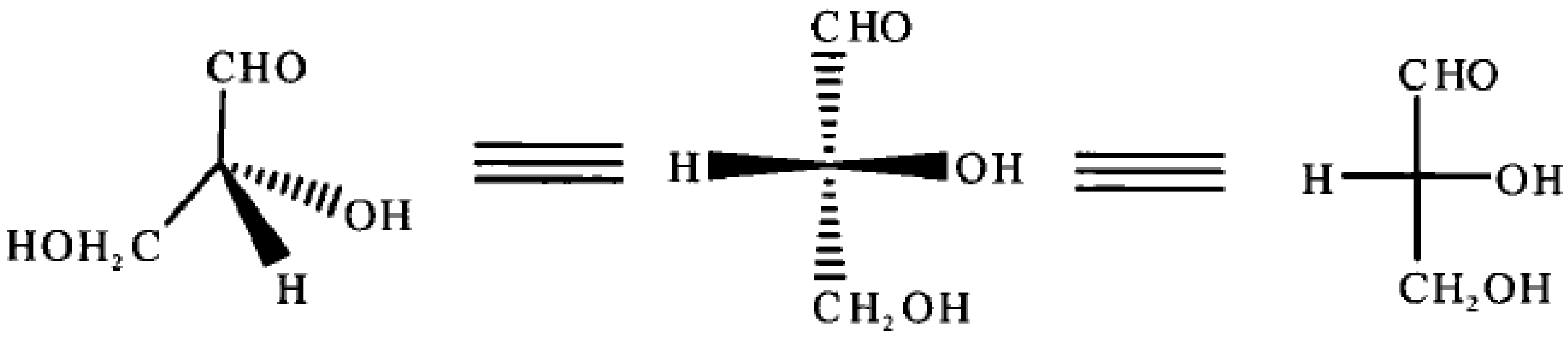


penta-2,3-diene



2,2′-dimethyl-6,6′-dinitro-1,1′-biphenyl

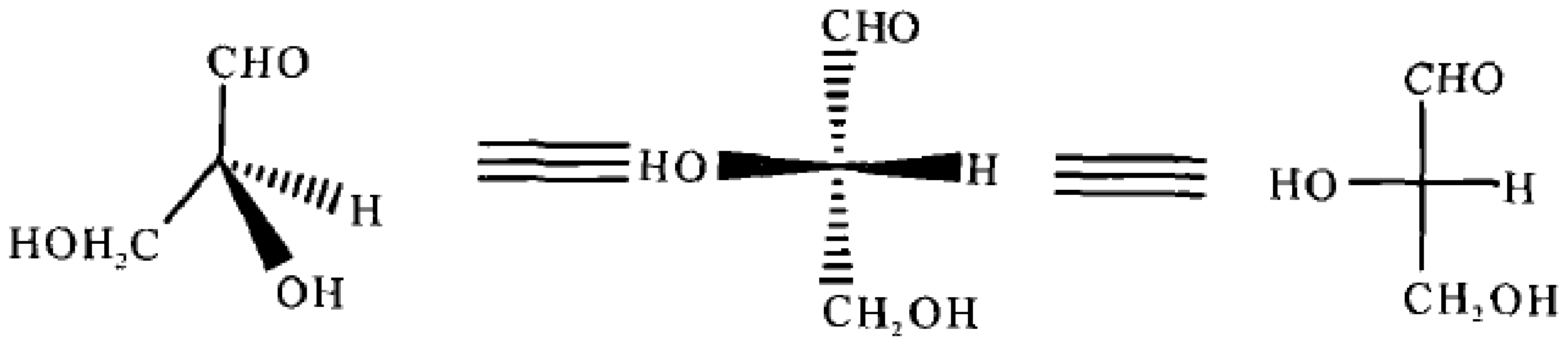
Fischer projection formulas can illustrate which stereoisomer of a compound is present. In a projection formula, a chiral carbon is placed in the center of **a + pattern**. The **vertical lines** (carbon chain) point away from the viewer, and the substituents (hydrogen and hydroxyl) are drawn horizontally, the **horizontal lines** point towards the viewer. The examples below are **D-** and **L-**glyceraldehyde. Stereochemistry is the key to understanding **carbohydrate** structure. The projection formulas used by Fischer to represent stereochemistry in chiral molecules are particularly well-suited to studying carbohydrates.



R-(+)-glyceraldehyde

D-(+)-glyceraldehyde

Fisher Projection

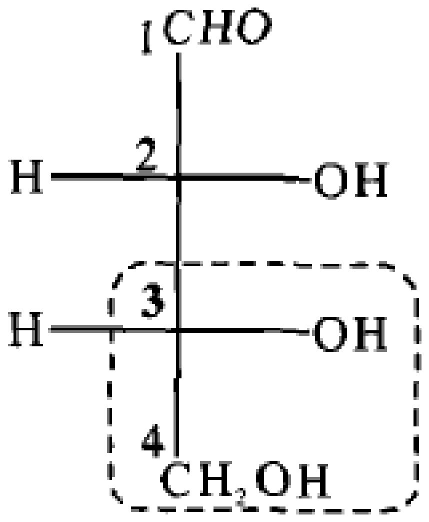


S-(−)-glyceraldehyde

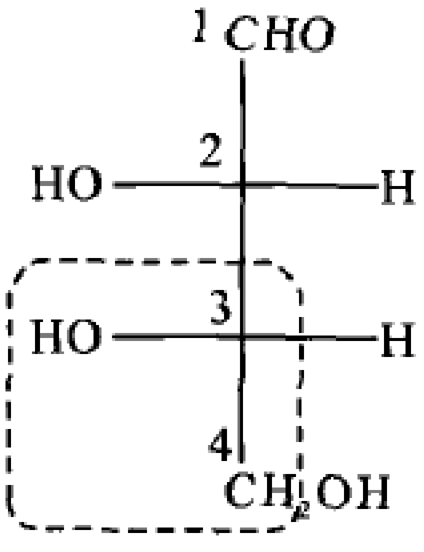
L-(−)-glyceraldehyde

Fisher Projection

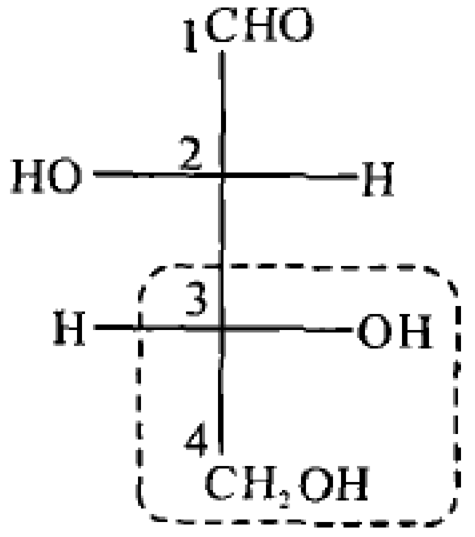
Two stereochemical descriptors were defined: **D** and **L**. The **absolute configuration** of (+)-**glyceraldehyde** was said to be **D** and that of its enantiomer, (−)-**glyceraldehyde**, **L**. Compounds that had a spatial arrangement of substituents analogous to D-(+)- and L-(−)-glyceraldehyde were said to have the D and L configurations, respectively. Relative to each other, both hydroxyl groups are on the same side in Fischer projections of the erythrose enantiomers. The remaining two stereoisomers have hydroxyl groups on opposite sides in their Fischer projection. They are **diastereomers** of D- and L-erythrose and are called D- and L *-threose*. The prefixes **D** and **L** show that the configuration at the **highest numbered stereogenic center** is analogous to that of D-(−)-glyceraldehyde (the hydroxyl of the **highest numbered stereogenic center** is on the right side of the chain) or L-(−)-glyceraldehyde (the hydroxyl of the **highest numbered stereogenic center** is on the left side of the chain).



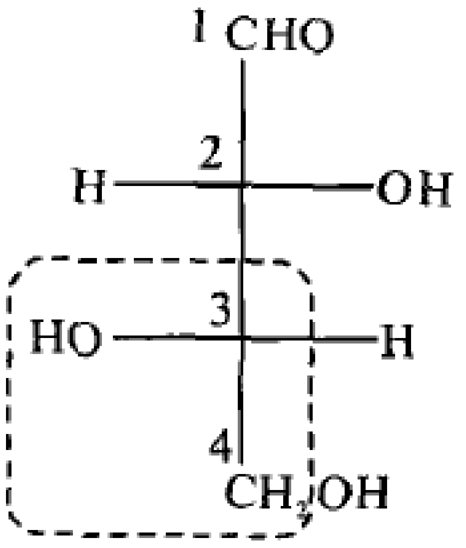
D-erythrose



L-erythrose



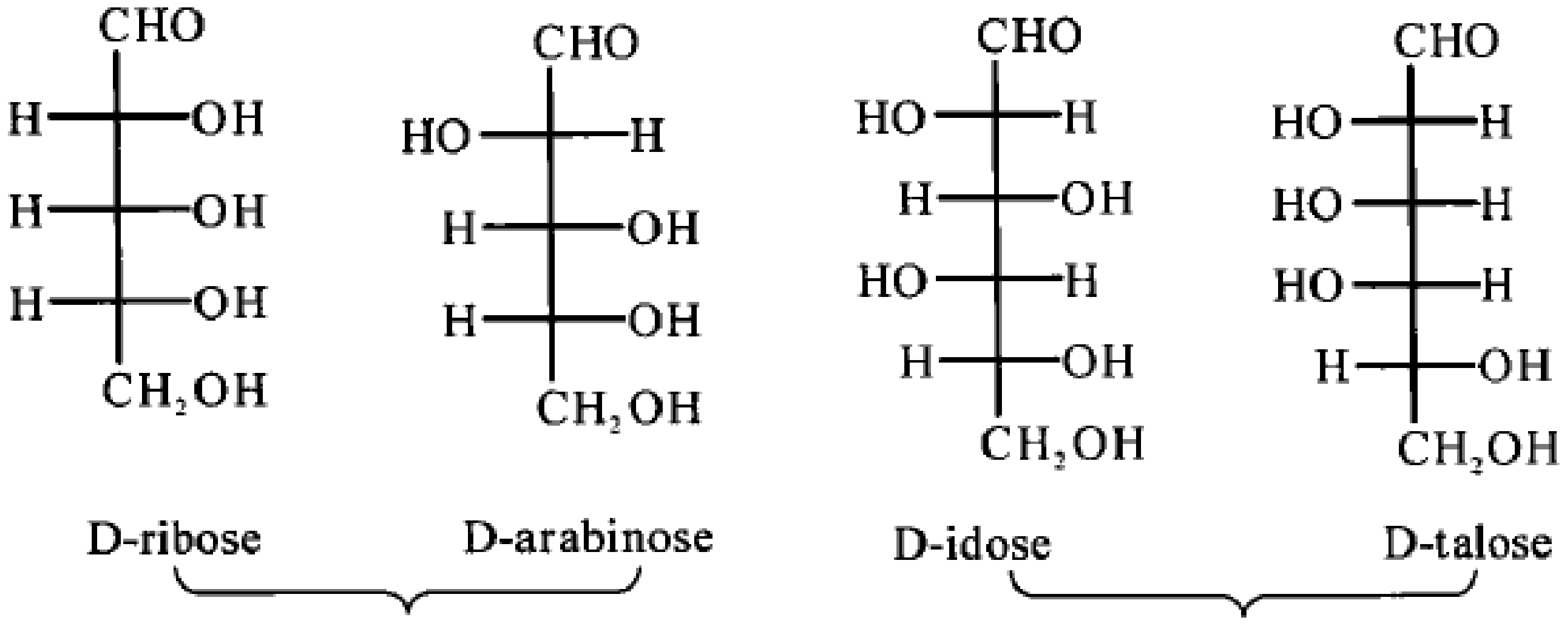
D-threose



L-threose

Fischer projections and D-L notation have proved to be so helpful in representing carbohydrate stereochemistry that the chemical and the biochemical literature is replete with their use. But the use of **D** and **L** is gradually being replaced by the **R** and **S** system of designating isomers, which is particularly useful when more than one chiral carbon atom is present.

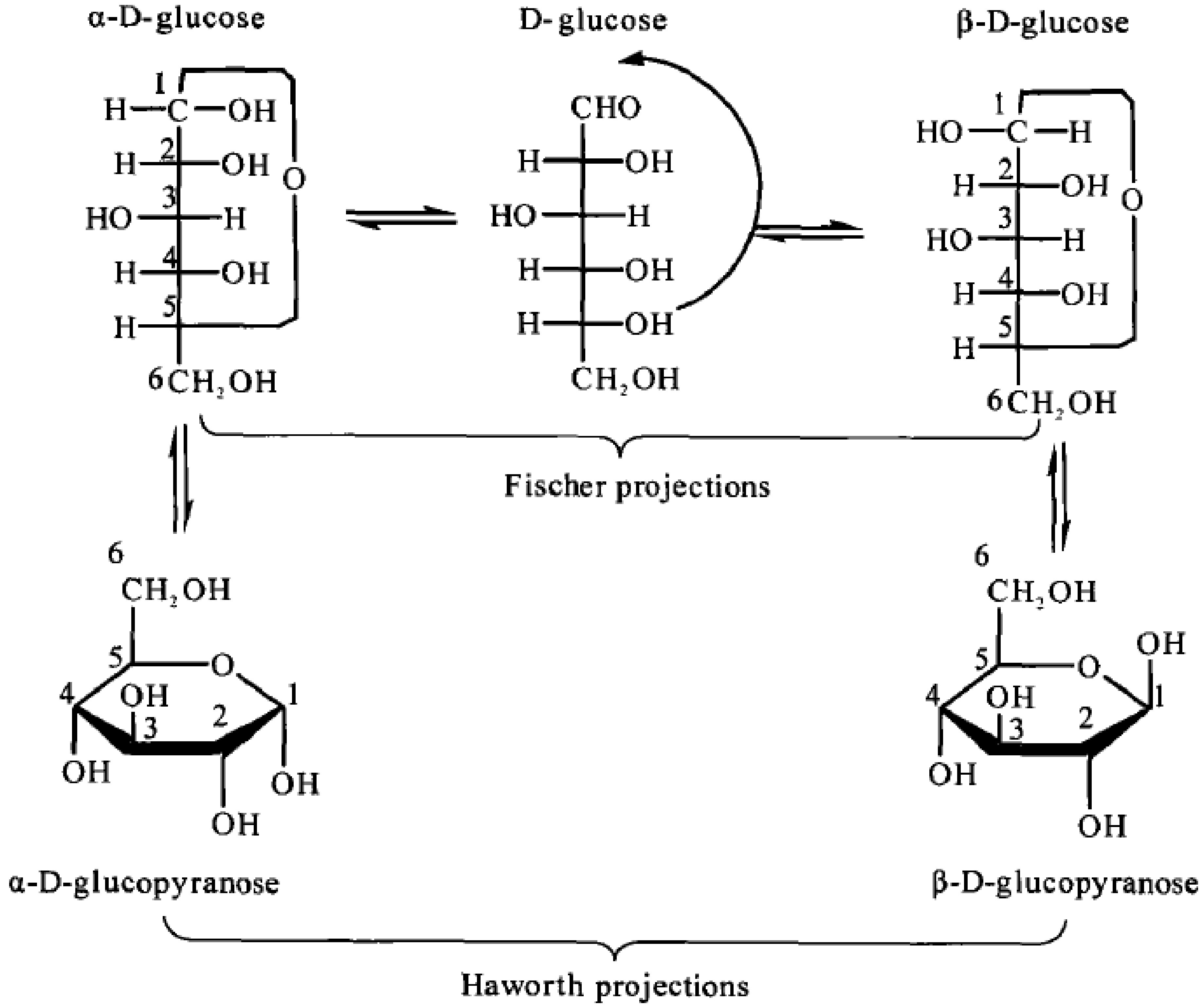
Diastereomers that differ in configuration at only one asymmetric carbon are called **epimers**. For example, D-ribose and D-arabinose are C-2 epimers (they differ in configuration only at C-2), and D-idose and D-talose are C-3 epimers.



D-ribose D-arabinose D-idose D-talose

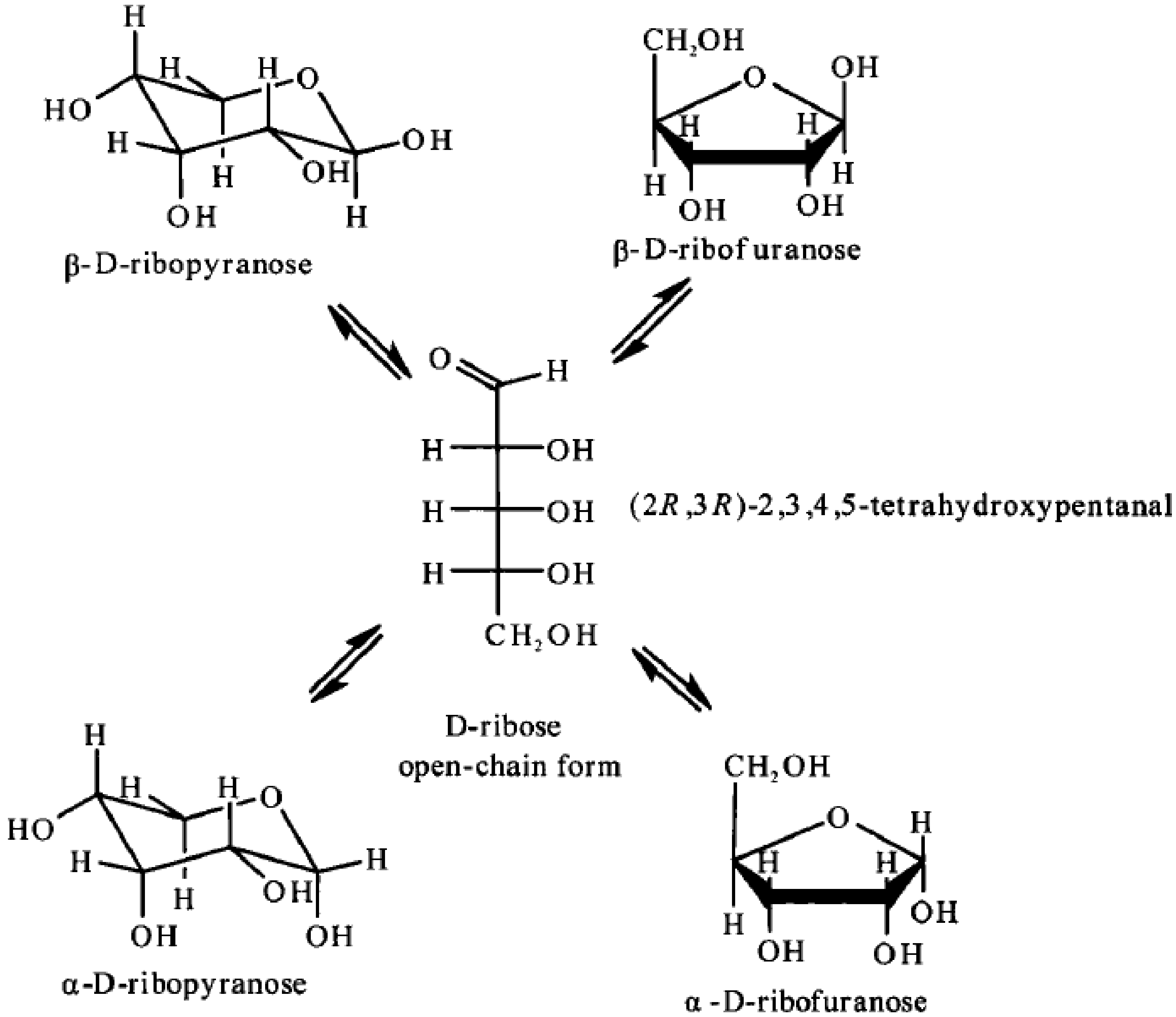
C-2 epimers. C-3 epimers.

An aldehyde of sugar reacts with one molecule of an alcohol to give a **hemiacetal**, and with a second molecule of the alcohol to give an **acetal**. Fischer projections are not the best way to show the structure of a cyclic sugar. The cyclic structure of carbohydrates is often drawn in the **Haworth projection**, which depicts the ring as being flat (of course, it is not). In a Haworth projection of a D-pyranose, the six-membered ring is represented as flat and is viewed edge on. The ring oxygen is always placed in the back right-hand corner of the ring, with the anomeric carbon (C-1) on the right-hand side and the primary alcohol group drawn up from the back left-hand corner (C-5). Groups on the right in a Fischer projection are down in a Haworth projection, whereas groups on the left in a Fischer projection are up in a Haworth projection.



The change from one form to an equilibrium mixture of all the possible hemiacetals causes a change in optical rotation called **mutarotation.** **Cyclic hemiacetal** formation is most common when the ring that results is five- or six-membered. Since six-membered rings are normally less strained than five-membered ones, **pyranose forms** are usually present in greater amounts than **furanose forms** at equilibrium, and the concentration of the open-chain form is quite small. For example, the **D-ribose**, also called (2R,3R)-2,3,4,5-tetrahydroxypentanal, can interconvert between **furanose** and **pyranose** forms and between the **α** and the **β configuration** of each form: β-D-Ribopyranose (56%); β-D-Ribofuranose (18%); α-D-Ribopyranose (20%); α-D-Ribofuranose (6%) and open-chain form (<1%).

Anomers are two sugars that differ in configuration only at the new stereogenic center formed from the carbonyl carbon in the open-chain form. This carbon is called **anomeric carbon**. The anomeric carbon is the only carbon in the molecule that is bonded to two oxygens. The prefixes **α and β** denote the configuration about the anomeric carbon. Anomers, like **epimers**, are a

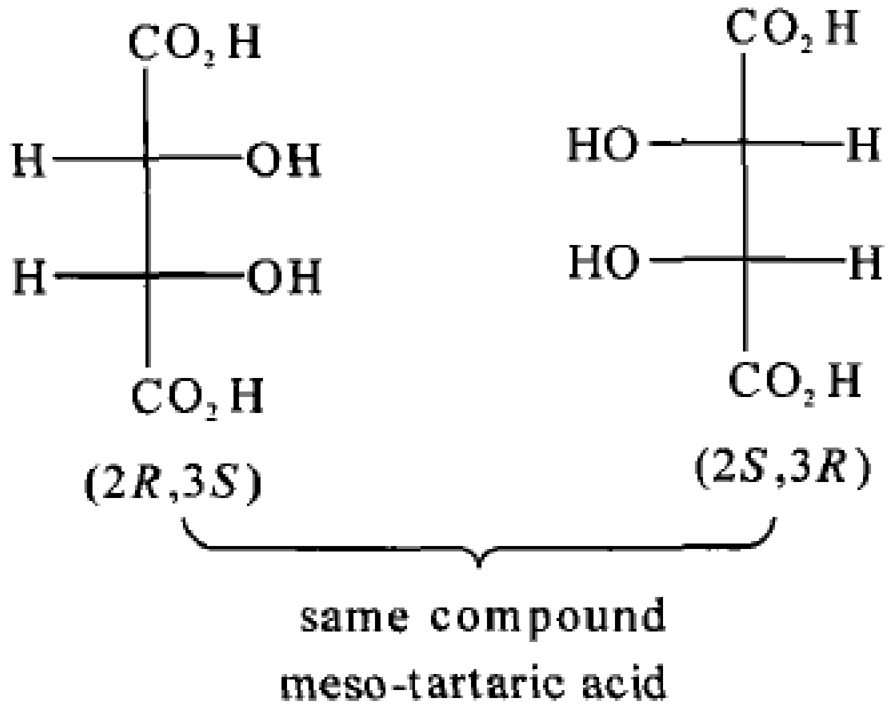


particular kind of diastereomers—they differ in configuration at only one carbon atom. For example, α-D-ribopyranose and β-D- ribopyranose are called anomers. The configuration of the anomeric carbon is *α* when its hydroxyl group is on the same side of a Fischer projection as the hydroxyl group at the highest numbered stereogenic center. When the hydroxyl groups at the anomeric carbon and the highest numbered stereogenic center are on opposite sides of a Fischer projection, the configuration at the anomeric carbon is *β*.

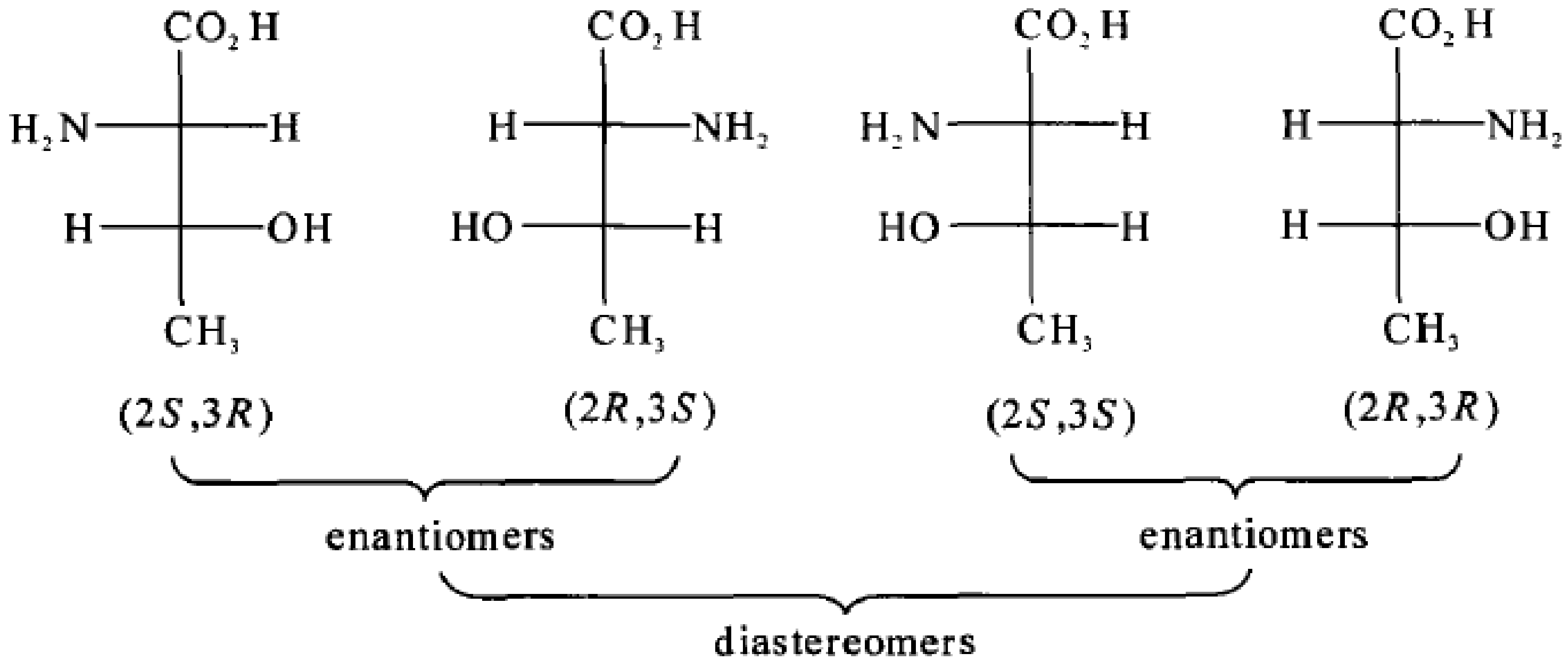
A **meso** structure has two identical asymmetric centers and a plane of symmetry. The mirror images are superimposable and optical isomers are not possible. This molecule is called a **meso isomer**.

A mixture of equal amounts of two enantiomers is called a **racemic mixture** or a **racemate**. Racemic mixtures do not rotate the plane of polarized light.

Diastereomers have the same molecular formula and sequence of bonded elements but different spatial arrangements and are nonsuperimposable, non-



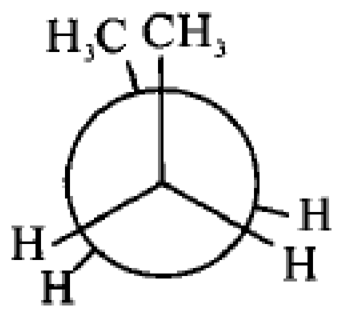
mirror images. Diastereomers are different molecules having different chemical and physical properties.



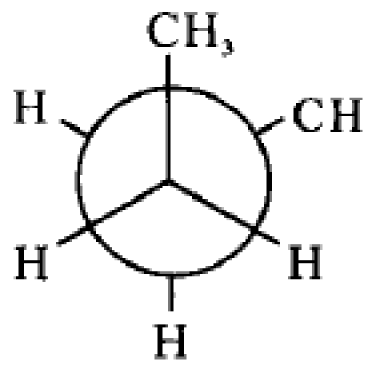
5.4.3 Conformational Isomers

Conformational isomers are different shapes of the same molecule resulting from rotation round C—C single bonds. Conformational isomers are not different compounds and are freely interconvertable.

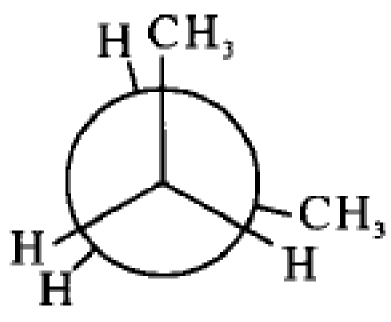
Alkanes can take up different shapes or conformations due to rotation around the C—C bonds. Actually there are an infinite number of conformational isomers (also called conformations) because there are an infinite number of degrees of rotation around the bond, but normally one only needs to be concerned with energy minima and maxima. **The most stable conformations are those where the bonds are staggered, rather than eclipsed.** The torsional angle in butane is the angle between the first and the third C—C bonds when viewed along the middle C—C bond. The most stable conformation of butane has a torsional angle of 180° where the carbon atoms and the C—C bonds are as far apart from each other as possible. The other possible staggered conformation has a torsional angle of 60° which results in some steric and electronic strain — called a **gauche interaction.** The most stable conformation for a straight chain alkane is ***zigzag*** shaped where all the torsional angles are at 180°. Organic compounds commonly exist as rapidly interconverting chiral conformations. For example, butane exists in gauche conformations that are chiral, but they quickly interconvert. They are in equilibrium with the totally anti conformation, which is symmetric, however, when we speak of chirality, we intend to focus on observable, persistent properties rather than transient conformations, implying that butane must be achiral.



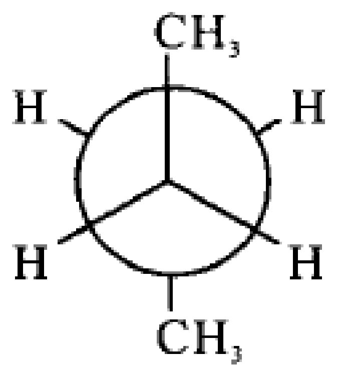
eclipsed-0°
achiral



gauche-60°
chiral

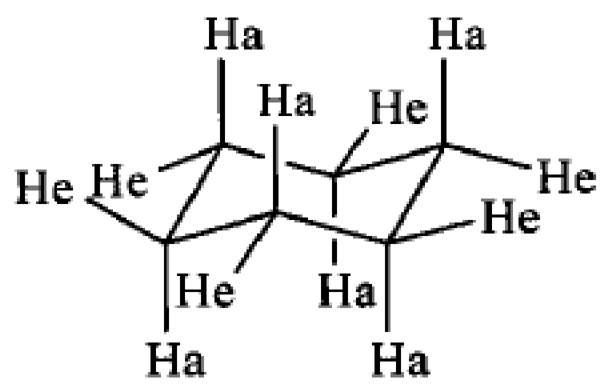


eclipsed-120°
chiral



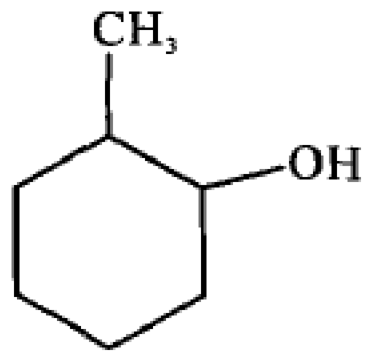
anti-180°
achiral

Cycloalkanes can adopt different conformations or shapes. The most stable conformation for cyclohexane is the *chair*. Each carbon in the chair has two C—H bonds, one of which is **equatorial** and one of which is **axial**. A chair structure can invert through a high energy boat intermediate such that the equatorial bonds become axial and the axial bonds become equatorial. If a substituent is present, the most stable chair conformation is where the substituent is equatorial. In the axial position, the substituent experiences two gauche interactions with C—C bonds in the ring. Substituted cycloalkanes can also exist as configurational isomers.

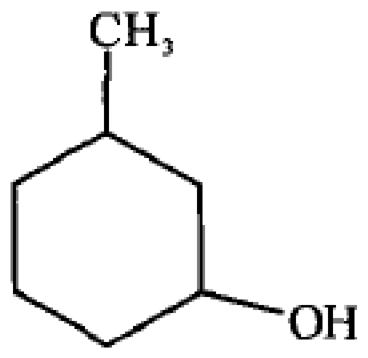


When more than one group are attached to cyclohexane, the stereoisomeric possibilities increase. These possibilities are shown for methylcyclohexanol as follows:

structural isomers:

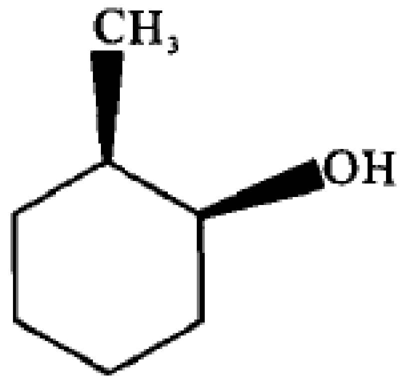


2-methylcyclohexanol

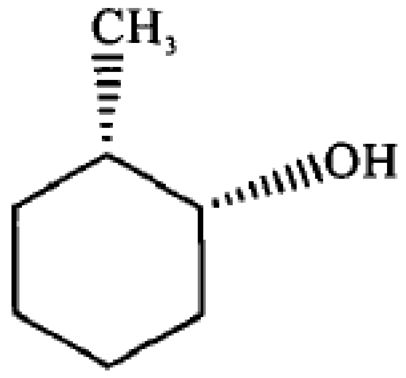


3-methylcyclohexanol

R,S isomers:

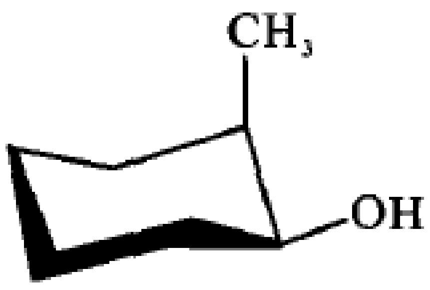


(1*S*,2*R*)-2-methylcyclohexanol



(1*R*,2*S*)-2-methylcyclohexanol

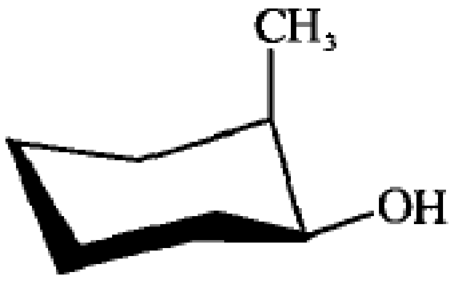
cis-trans isomers:



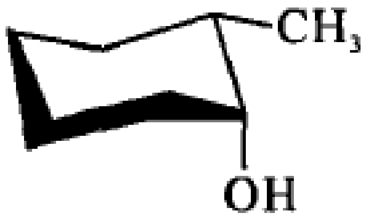
cis-2-methylcyclohexanol

trans-2-methylcyclohexanol

conformational isomers:



cis-2-methylcyclohexanol



cis-2-methylcyclohexanol

References

[1] Meislich H, Nechamkin H, Sharefkin. Schaum's easy outlines. Organic chemistry [M]. New York: McGraw - Hill Professional, 2000.

[2] Patrick G L. Instant notes organic chemistry [M]. New York: Garland Science/BIOS Scientific Publishers, 2004.

[3] Ernest L E, Samuel H W, Lewis N M. Stereochemistry of organic compounds [M]. New York: John Wiley & Sons, Inc., 1994.

[4] Michael E. Organic reaction mechanisms: second edition [M]. London: Taylor & Francis Inc., 2004.

[5] Hoffman R V. Organic chemistry: an intermediate text: second edition [M]. New Jersey: John Wiley & Sons Inc., 2004.

[6] Carey F A. Organic chemistry: fourth edition [M]. New York: The McGraw - Hill Company, 2000.

[7] Clayden J, Geeves N, Warren S. Organic Chemistry [M]. Oxford: Oxford University Press, 2000.

[8] McMurry J. Organic chemistry: seventh edition [M]. Belmont: Thomson learning Inc., 2008.

[9] McMurry J, Simanek E. Fundamentals of organic chemistry: sixth edition [M]. Belmont: Thomson learning Inc., 2007.

Chapter 6 Physical Chemistry

6.1 Introduction

Physical chemistry is the branch of chemistry that establishes and develops the principles of the subject. It is the explanation of macroscopic, microscopic, atomic, subatomic and particulate phenomena in chemical systems in terms of physical concepts; sometimes using the principles, practices and concepts of physics like *thermodynamics*, *kinetics*, *quantum chemistry* and *statistical mechanics*. Physical chemistry is also essential for developing and interpreting the modern techniques used to determine the structure and properties of matter, such as new synthetic materials and biological macromolecules.

Since physical chemistry is a discipline which is concerned with the theoretical and the quantitative basis of chemistry, the practitioner of every discipline of chemistry must be familiar with physical chemistry in order to understand his own subject. Similarly physical chemistry is necessary for a geologist, metallurgist, biologist and an engineer. Without doubt as it is confessed by many eminent physical chemists, physical chemistry is a difficult subject as a lot of mathematics and physics is applied in its elucidation which tends to make the subject abstract. Hence a course in physical chemistry should avoid excessively mathematical treatment that would obscure the physical ideas and at the same time the treatment should not be so qualitative as to mask its conceptual logic. The conceptual logic and beauty of physical chemistry will be evident only if the subject is presented with mathematical precision without losing sight of physical reality. Secondly, at present the domain of physical chemistry is not confined to thermodynamics and kinetics alone but encompasses a wide range of topics such as quantum mechanics, spectroscopy, statistical mechanics, electrochemistry, photochemistry, macromolecules. Consequently, a single course in which such varied areas are treated can be valuable if it provides coherence to the study of these different topics by providing a conceptual link among them.

At its most basic level, physical chemistry is the theoretical and experimental foundation for the field of chemistry. Using the concepts of physical chemistry, one can, in principle, predict the outcome of any chemical transformation or reaction. Physical chemistry has many connections to each of the other branches of chemistry, including biochemistry. Physical chemistry also has strong connections to physics, and many topics within physical chemistry are discussed in physics courses.

Physical chemistry can also be subdivided based on size of the sample being studied. One can start with the smallest chemical entity, the *atom*, and discuss its structure and properties. The next size up, *molecule*, can also be discussed in terms of structure of individual molecule and interactions between molecules. On the other hand, classical thermodynamics deals with larger amounts: on the order of a mole of a substance. In fact, classical thermodynamics does not depend on the existence of atoms. However, there are important connections between very small numbers of atoms and the bulk substance. One of these connections is *statistical thermodynamics*, which deals with the behavior of larger groups of individual entities (such as atoms) in a probabilistic sense. Another important connection is *kinetics*, which includes the very important "detail" time. One can study the kinetics of a bulk reaction to propose a *mechanism* (i.e. the sum of individual atomic or molecular transformations) for the reaction, thus yielding crucial information about what is happening on the nanoscale.

The foundation of modern physical chemistry is thought to have been laid in the 1860s to 1880s by work on chemical thermodynamics, electrolytes in solutions, chemical kinetics and other subjects. One milestone was the publication in 1876 by J. W. Gibbs of his paper, *On the Equilibrium of Heterogeneous Substances*, which contained several of the cornerstones of physical chemistry, such as Gibbs energy, chemical potentials, Gibbs phase rule and subsequent naming and accreditation of enthalpy to H. K. Onnes and to macromolecular processes.

The first scientific journal for publications specifically in the field of physical chemistry was the German journal founded in 1887 by W. Ostwald and J. H. Van't Hoff, who were two of the other leading figures of physical chemistry in the late 19th century and early 20th century together with S. A. Arrhenius. All three were awarded with the Nobel Prize in Chemistry in the period 1901 – 1909.

Developments in the following decades include the application of statistical mechanics to chemical systems and work on *colloids* and *surface chemistry*, where I. Langmuir made many contributions. Another important step was the development of *quantum mechanics* into *quantum chemistry* from the 1930s, where L. Pauling was one of the leading names. Theoretical developments have gone hand in hand with developments in experimental methods, where the use of different forms of spectroscopy, such as *infrared spectroscopy*, *microwave spectroscopy*, *EPR spectroscopy* and *NMR spectroscopy*, is probably the most important 20th century development.

Further development in physical chemistry may be attributed to discoveries in *nuclear chemistry*, especially in isotope separation, more recent discoveries in *astrochemistry* and *surface chemistry*, as well as the development of calculation algorithms in field of additive physicochemical properties, including all of physicochemical properties, such as boiling point, critical point, surface tension, vapor pressure etc. These parameters can be precisely calculated from chemical structure, even if such chemical molecule is still non existent, and in this area it is concentrated practical importance of contemporary physical chemistry.

6.2 Thermodynamics

In science, **thermodynamics** (from the Greek *therme*, meaning *heat*, and *dynamis*, meaning *force*) is the study of energy conversion between *heat* and *mechanical work*, and subsequently the macroscopic variables such as *temperature*, *volume* and *pressure*. Like all sciences, the basis of thermodynamics is experimental observation. In thermodynamics these findings have been formalized into certain basic laws, which are known as the *first*, the *second*, and the *third law of thermodynamics*. In addition to these laws, the *zeroth law of thermodynamics*, which in the logical development of thermodynamics precedes the first law, has been set forth.

6.2.1 Laws of Thermodynamics

The starting point for the most thermodynamic considerations are the **laws of thermodynamics**, which postulate that energy can be exchanged between physical systems as *heat* or *work*. They also postulate the existence of a quantity named **entropy**, which can be defined for any isolated system that is in thermodynamic equilibrium. In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of *system* and *surroundings*. A **system** is composed of particles, whose average motions define its properties, which in turn are related to one another through equations of state. Properties can be combined to express *internal energy* and *thermodynamic potentials*, which are useful for determining conditions for *equilibrium* and *spontaneous processes*.

With these tools, the usage of thermodynamics describes how systems respond to changes in their *surroundings*. This can be applied to a wide variety of topics in science and engineering, such as engines, phase transitions, chemical reactions, transport phenomena, and even black holes. The results of thermodynamics are essential for other fields of physics and for chemistry, chemical engineering, aerospace engineering, mechanical engineering, cell biology, biomedical engineering, materials science, and even economics.

In thermodynamics, there are four laws that do not depend on the details of the systems under study or how they interact. Hence these laws are very generally valid, can be applied to systems about which one knows nothing other than the balance of energy and matter transfer. Examples of such systems include Einstein's prediction, around the turn of the 20th century, of spontaneous emission, and ongoing research into the thermodynamics of black holes. These four laws are:

1. Zeroth Law of Thermodynamics, about Thermal Equilibrium

If two thermodynamic systems are separately in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

If we grant that all systems are (trivially) in thermal equilibrium with themselves, the **Zeroth law** implies that thermal equilibrium is an equivalence relation on the set of thermodynamic systems. This law is tacitly assumed in every measurement of temperature. Thus, if we want to know if two bodies are at the same temperature, it is not necessary to bring them into contact and to watch whether their observable properties change with time.

This law was considered so obvious it was added as a virtual afterthought, hence the designation Zeroth, rather than Fourth. In short, if the temperature of material A is equal to the temperature of material B, and B is equal to the temperature of material C. then A and C must also be equal.

2. First Law of Thermodynamics, about the Conservation of Energy

The change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to or removed from the system and the work done on or by the system. So, we can say (1) "*Energy is neither created nor destroyed*" and (2) "*There is no free lunch*".

3. Second Law of Thermodynamics, about Entropy

The total entropy of any isolated thermodynamic systems always increases over time, approaching a maximum value or we can say, "*In an isolated system, the entropy never decreases*". Another way to phrase this: "*Heat cannot spontaneously flow from a colder location to a hotter area* — work is required to achieve this."

4. Third Law of Thermodynamics, about the Absolute Zero of Temperature

As a system asymptotically approaches absolute zero of temperature all processes virtually cease and the entropy of the system asymptotically approaches a minimum value; also stated as: "*the entropy of all systems and of all states of a system is smallest at absolute zero*" or equivalently "*it is impossible to reach the absolute zero of temperature by any finite number of processes*". Absolute zero, at which all activity would stop if it were possible to happen, is −273.15 ℃ (degrees Celsius), or −459.67 ℉ (degrees Fahrenheit) or 0 K (kelvins, formerly sometimes degrees absolute).

6.2.2 Thermodynamic Potentials

As can be derived from the *energy balance equation* (or *Burk's equation*) on a thermodynamic system there exist energetic quantities called **thermody-**

namic potentials, being the quantitative measure of the stored energy in the system. The five most well known potentials are:

Internal energy	$U = TS - pV$
Helmholtz free energy	$A = U - TS$
Enthalpy	$H = U + pV$
Gibbs free energy	$G = U + pV - TS$
Grand potential	$\Phi_G = U - TS - \mu N$

Other thermodynamic potentials can be obtained through *Legendre transformation*. Potentials are used to measure energy changes in systems as they evolve from an initial state to a final state. The potential used depends on the *constraints* of the system, such as constant temperature or pressure. **Internal energy** is the internal energy of the system, **enthalpy** is the internal energy of the system plus the energy related to pressure-volume work, and **Helmholtz** and **Gibbs energy** are the energies available in a system to do useful work when the temperature and the volume or the pressure and the temperature are fixed, respectively.

6.2.3 Thermodynamic System and Processes

An important concept in thermodynamics is the "system". A **system** is the region of the universe under study. Everything in the universe except the system is known as **surroundings**. For an engine, a fixed boundary means the piston is locked at its position; as such, a constant volume process occurs. In that same engine, a moveable boundary allows the piston to move in and out. For closed systems, boundaries are real while for open system boundaries are often imaginary. There are five dominant classes of systems:

(1) *Isolated* systems — matter and energy may not cross the boundary

(2) *Adiabatic* systems — heat must not cross the boundary

(3) *Diathermic* systems — heat may cross boundary

(4) *Closed* systems — matter may not cross the boundary

(5) *Open* systems — heat, work, and matter may cross the boundary (often called a control volume in this case)

As time passes in an isolated system, internal differences in the system tend to even out and pressures and temperatures tend to equalize, as do density differences. A system, in which all equalizing processes have gone practically to completion, is considered to be in a state of *thermodynamic equilibrium*.

In thermodynamic equilibrium, a system's properties are, by definition, unchanging in time. Systems in equilibrium are much simpler and easier to understand than systems which are not in equilibrium. Often, when analyzing a thermodynamic process, it can be assumed that each intermediate state in the process is at equilibrium. This will also considerably simplify the situation. Thermodynamic processes which develop so slowly as to allow each intermediate step to be an equilibrium state are said to be *reversible processes*.

When a system is at equilibrium under a given set of conditions, it is said to be in a *definite state*. The thermodynamic state of the system can be described by a number of *intensive variables* and *extensive variables*. The properties of the system can be described by an *equation of state* which specifies the relationship between these variables. State may be thought of as the instantaneous quantitative description of a system with a set number of variables held constant.

A **thermodynamic process** may be defined as the energetic evolution of a thermodynamic system proceeding from an initial state to a final state. Typically, each thermodynamic process is distinguished from other processes, in energetic character, according to what parameters, as temperature, pressure, or volume, etc., are held fixed. Furthermore, it is useful to group these processes into pairs, in which each variable held constant is one member of a conjugate pair. The seven most common thermodynamic processes are shown below:

(1)An *isobaric* process occurs at constant pressure.

(2) An *isochoric* process, or *isometric/isovolumetric* process, occurs at constant volume.

(3)An *isothermal* process occurs at a constant temperature.

(4)An *adiabatic* process occurs without loss or gain of energy by heat.

(5)An *isentropic* process (reversible adiabatic process) occurs at a constant entropy.

(6)An *isenthalpic* process occurs at a constant enthalpy.

(7)A *steady state* process occurs without a change in the internal energy of a system.

6.3 Phase Equilibrium

Phase equilibrium studies the various situations in which two or more phases which can coexist in thermodynamic equilibrium with each other, the nature of the transitions between phases, and the effects of temperature and pressure upon these equilibria. Many superficial aspects of the subject are largely qualitative, for example, the empirical classification of types of *phase diagrams*; but the basic problems always are susceptible to quantitative thermodynamic treatment, and in many cases, statistical thermodynamic methods can be applied to simple molecular models.

For example, water in a closed jar with an air space over it forms a two phase system. Most of the water is in the liquid phase, where it is held by the mutual attraction of water molecules. Even at equilibrium molecules are constantly in motion and, once in a while, a molecule in the liquid phase gains enough kinetic energy to break away from the liquid phase and enter the gas phase. Likewise, every once in a while a vapor molecule collides with the liquid surface and condenses into the liquid. At equilibrium, *evaporation* and *condensation* processes exactly balance and there is no net change in the volume of either phase.

6.3.1 Phase

The **phase** is a region of space (a thermodynamic system), throughout which all physical properties of a material are essentially uniform. Examples of physical properties include *density*, *index of refraction* and *chemical composition*. A simple description is that a phase is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable. In a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air over the water is a third phase. The glass of the jar is another separate phase.

Distinct phases may be described as different states of matter such as *gas*, *liquid*, *solid* or *plasma*. Distinct phases may also exist within a given state of matter. As shown in the diagram for iron alloys, several phases exist for both the solid and liquid states. Phases may also be differentiated based on solubility as in *polar* or *non-polar*. A mixture of water (a polar liquid) and oil (a non-polar liquid) will spontaneously separate into two phases. Water has a very low solubility (is insoluble) in oil, and oil has a low solubility in water. Solubility is the maximum amount of a solute that can dissolve in a solvent before the solute ceases to dissolve and remains in a separate phase.

6.3.2 Phase Rule

Phase rule was proposed by J. W. Gibbs in the 1870s as the equality:

$$F = C - P + 2$$

Where P is the number of phases in thermodynamic equilibrium with each other and C is the number of components. Typical phases are solids, liquids and gases. A system involving one pure chemical is an example of a one-component system. Two-component systems, such as mixtures of water and ethanol, have two chemically independent components. F is the number of degrees of freedom, which means the number of intensive properties such as temperature or pressure, which are independent of other intensive variables.

For pure substances $C = 1$ so that $F = 3 - P$. In a single phase ($P = 1$) condition of a pure component system, two variables ($F = 2$), such as temperature and pressure, can be controlled to any selected pairs of values. However, if the temperature and the pressure combination ranges to a point where the pure component undergoes a separation into two phases ($P = 2$), F decreases from 2 to 1. When the system enters the two phase region, it becomes no longer possible to independently control temperature and pressure.

6.3.3 Phase Diagrams

A **phase diagram** is a type of chart used to show conditions at which thermodynamically distinct phases can occur at equilibrium. Common components of a phase diagram are lines of equilibrium or phase boundaries, which refer to lines that mark conditions under which multiple phases can coexist at equilibrium. *Phase transitions* occur along lines of equilibrium. **Triple points** are points on phase diagrams where lines of equilibrium intersect. Triple points mark conditions at which three different phases can coexist. For example, the water phase diagram has a triple point corresponding to the single temperature and pressure at which solid, liquid, and gaseous water can coexist in a stable equilibrium.

The *solidus* is the temperature below which the substance is stable in the solid state. The *liquidus* is the temperature above which the substance is stable in a liquid state. There may be a gap between the solidus and the liquidus; within the gap, the substance consists of a mixture of crystals and liquid.

The simplest phase diagrams are pressure-temperature diagrams of a single simple substance, such as water. The axes correspond to the pressure and the temperature. The phase diagram shows, in pressure-temperature space, the lines of equilibrium or phase boundaries between the three phases of solid, liquid, and gas.

In the phase diagram of water, the phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the **critical point**. This reflects the fact that, at extremely high temperatures and pressures, the liquid and the gaseous phases become indistinguishable, in what is known as a **supercritical fluid**.

Other much more complex types of phase diagrams can be constructed, particularly when more than one pure component is present. In that case concentration becomes an important variable. Phase diagrams with more than two dimensions can be constructed that show the effect of more than two variables on the phase of a substance. Phase diagrams can use other variables in addition to or in place of temperature, pressure and composition, for example the strength of an applied electrical or magnetic field and they can also involve substances that take on more than just three states of matter.

A simple example is the phase diagram with hypothetical components 1 and 2 in a *non -azeotropic* mixture. The fact that there are two separate curved lines joining the boiling points of the pure components means that the vapor composition is usually not the same as the liquid composition the vapor is in equilibrium with.

Another type of phase diagram plots temperature against the relative concentrations of two substances in a binary mixture called a *binary phase diagram*. Such a mixture can be a solid solution, *eutectic* or *peritectic*, among others. These two types of mixtures result in very different graphs. Another type of binary phase diagram is a *boiling point diagram* for a mixture of two components, i. e. chemical compounds. For two particular volatile components at a certain pressure such as atmospheric pressure, a boiling point diagram shows what vapor (gas) compositions are in equilibrium with given liquid compositions depending on temperature. In a typical binary boiling point diagram, temperature is plotted on a vertical axis and mixture composition on a horizontal axis.

6.4 Chemical Kinetics

Chemical kinetics is the study and discussion of chemical reactions with respect to *reaction rates*, *effect of various variables*, *re-arrangement of atoms*, *formation of intermediates* etc. It includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states that can describe the characteristics of a chemical reaction. In 1864, P. Waage and C. Guldberg pioneered the development of chemical kinetics by formulating the *law of mass action*, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

6.4.1 Rate of Reaction

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for *zero-order* reactions (for which reaction rates are independent of concentration), *first-order* reactions, and *second-order* reactions, and can be derived for others. In consecutive reactions the *rate-determining step* often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The *activation energy* for a reaction is experimentally determined through the *Arrhenius equation* and the *Eyring equation*.

This is the difference between thermodynamics and kinetics. Thermodynamics can tell you only that a reaction should go because the products are more stable (have a lower free energy) than the reactants. Another way of saying this is that the reaction has a negative free energy change: ΔG is negative and therefore the reaction is spontaneous. Yet another way of saying this is to say that the reaction has a large equilibrium constant, signifying that if nature could ever attain equilibrium, there would be many more products present than there are reactants. Notice that the $\Delta G = -RT\ln K$ equation says all this at once. Kinetics, on the other hand, can tell you how fast the reaction will go but doesn't tell you anything about the final state of things once it gets there. For example, at room temperature (a wide range of temperatures), thermodynamic data indicates that diamond shall convert to graphite, but in reality, the conversion rate is so slow that most people think that diamond is forever.

The main factors that influence the reaction rate include: the *physical state* of the reactants, the *concentrations* of the reactants, the *temperature* at which the reaction occurs, and whether or not any *catalysts* are present in the reaction.

6.4.2 Factors Affecting Reaction Rate

1. Nature of the Reactants

Depending upon what substances are reacting, the time varies. Acid reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influences the rate of its transformation into products. The reactions which involve lesser bond rearrangement proceed faster than the reactions which involve larger bond rearrangement.

2. Physical State

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact, in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches—one doesn't start with large logs right away.

3. Concentration

Concentration plays a very important role in reactions according to the collision theory of chemical reactions, because molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more frequently by being in closer contact at any given point in time. Think of two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants it causes these collisions to happen more often, increasing the reaction rate.

4. Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > Ea$) is significantly higher and is explained in detail by the Maxwell-Boltzmann distribution of molecular energies.

5. Catalyst

A **catalyst** is a substance that changes the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with a lower activation energy. In *autocatalysis* a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called *enzymes*. *Michaelis-Menten kinetics* describes the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibria, as the catalyst speeds up the backward and forward reactions equally.

6. Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the *partial pressure* of the gas. This is similar to the effect of increasing the concentration of a solution.

6.4.3 Applications

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and the pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.

6.5 Electrochemistry

Electrochemistry is a branch of chemistry concerned with the relation between electricity and chemical change. If a chemical reaction is driven by an external applied voltage, as in *electrolysis*, or if a voltage is created by a chemical reaction as in a battery, it is an *electrochemical reaction*. In contrast, chemical reactions where electrons are transferred between molecules are called *oxidation/reduction (redox) reactions*. In general, electrochemistry deals with situations where oxidation and reduction reactions are separated in space or time, connected by an external electric circuit to understand each process. Main applications of electrochemistry are described below.

6.5.1 Battery

An **electrochemical cell** is a device that produces an electric current from energy released by a spontaneous redox reaction. This kind of cell includes the *Galvanic cell* or *Voltaic cell*, named after L. Galvani and A. Volta, both scientists who conducted several experiments on chemical reactions and electric current during the late 18th century.

Electrochemical cells have two conductive electrodes (the *anode* and the *cathode*). The **anode** is defined as the electrode where oxidation occurs and the **cathode** is the electrode where the reduction takes place. Electrodes can be made from any sufficiently conductive materials, such as metals, semiconductors, graphite, and even conductive polymers. In between these electrodes is the electrolyte, which contains ions that can freely move.

An *electrical battery* is a combination of two or more electrochemical cells used to convert stored chemical energy into electrical energy. Since the invention of the first battery in 1800, batteries have become a common power source for many household and industrial applications.

There are two types of batteries: (1) *primary batteries* (disposable batteries), which are designed to be used once and discarded when they are exhausted, such as zinc-carbon batteries and alkaline batteries. (2) *secondary batteries* (rechargeable batteries), which are designed to be recharged and used multiple times. Batteries cells of this type (in order of increasing power density and cost) include nickel-cadmium (Ni-Cd), nickel-zinc (Ni-Zn), nickel metal hydride (Ni-MH) and lithium-ion (Li-ion) Batteries. Miniature cells are used to power devices such as hearing aids and wristwatches; larger batteries provide standby power for telephone exchanges or computer data centers.

6.5.2 Electrodeposition

The most important type of chemical reaction brought about by the passage of electric current is the deposition of a metal at a cathode from a solution of its ions. *Electroforming* is a variety of electrodeposition in which an article to be reproduced is rendered conductive by spraying a thin metallic coating, then *electroplated* with a metallic deposit that is stripped from its substrate and filled with backing to reproduce the original article. *Electrowinning* is used for the commercial production of active metals, such as aluminum, magnesium, and sodium, from molten salts and others, such as copper, manganese, and antimony, from aqueous solution. *Electrorefining* is commonly used to purify metals such as silver, lead, and copper. The impure metal is used as the anode, and purified metal is deposited at the cathode.

6.5.3 Electrolysis

The spontaneous redox reactions of a conventional battery produce electricity through the different chemical potentials of the cathode and the anode in the electrolyte. But in chemistry and manufacturing, *electrolysis* is a method of using a direct electric current to drive an otherwise non-spontaneous chemical reaction. Usually it is carried out in an electrolytic cell consisting of separated positive and negative electrodes (anode and cathode, respectively) immersed in an electrolyte solution containing ions or in a molten ionic compound. Reduction occurs at the cathode, where electrons are added that combine with positively charged cations in the solution. Oxidation occurs at the anode, where negatively charged anions give up electrons. Both thus become neutral molecules. Electrolysis is used extensively in metallurgy to extract or purify metals from ores or compounds and to deposit them from solution (*electroplating*). Electrolysis of molten sodium chloride yields metallic sodium and chlorine gas; that of a strong solution of sodium chloride in water (brine) yields hydrogen gas, chlorine gas, and sodium hydroxide (in solution); and that of water (with a low concentration of dissolved sodium chloride or other electrolyte) yields hydrogen and oxygen.

6.5.4 Prevention of Corrosion

Corrosion is the term applied to steel rust caused by an electrochemical process. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Formation of an oxide of iron due to oxidation of the iron atoms in solid solution is a well-known example of electrochemical corrosion, commonly known as *rusting*. This type of damage typically produces oxide(s) and/or salt(s) of the original metal. Some metals are more intrinsically resistant to corrosion than others, either due to the fundamental nature of the electrochemical processes involved or due to the details of how reaction products form. If a more susceptible material is used, many electrochemical techniques can be applied during manufacture process and use to protect its materials from damage, such as *passivation*, *plating* and *cathodic protection*.

6.6 Surface and Colloid Chemistry

6.6.1 Surface Science

Surface science is the study of physical and chemical phenomena that occur at the interface of two phases, including solid-liquid interfaces, solid-gas interfaces, solid-vacuum interfaces, and liquid-gas interfaces. It includes the fields of *surface chemistry* and *surface physics*. Some related practical applications are classed as *surface engineering*. The science encompasses concepts such as heterogeneous catalysis, semiconductor device fabrication, fuel cells, self-assembled monolayers (SAMs), and adhesives. Surface science is closely related to *interface* and *colloid science*. Interfacial chemistry and physics are common subjects for both, but the methods are different. In addition, interface and colloid science studies macroscopic phenomena that occur in heterogeneous systems due to peculiarities of interfaces.

Surface physics can be roughly defined as the study of physical changes that occur at interfaces. It overlaps with surface chemistry. Some of the things investigated by surface physics include surface states, surface diffusion, surface reconstruction, surface phonons and plasmons, epitaxy and surface enhanced Raman scattering, the emission and tunneling of electrons, spintronics, and the self-assembly of nanostructures on surface.

6.6.2 Surface Chemistry

Surface chemistry can be roughly defined as the study of chemical reactions at interfaces. It is closely related to surface engineering, which aims at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface. Surface chemistry also overlaps with electrochemistry. Surface science is of particular importance to the field of heterogeneous catalysis.

The adhesion of gas or liquid molecules to the surface is known as *adsorption*. This can be due to either *chemisorption* or *physisorption*. These two are included in surface chemistry. The behavior of a solution based interface is affected by the surface charge, dipoles, energies, and their distribution within the electrical double layer.

6.6.3 The Surface Analysis Techniques

The surface analysis techniques involve both physical and chemical analysis techniques. Several modern methods probe the topmost 1 - 10 nm of the surfaces exposed to vacuum. These include X-ray photoelectron spectroscopy, Auger electron spectroscopy, low-energy electron diffraction, electron energy loss spectroscopy, thermal desorption spectroscopy, ion scattering spectroscopy, secondary ion mass spectrometry, and other surface analysis methods included in the list of materials analysis methods. Many of these techniques require vacuum as they rely on the detection of electrons or ions emitted from the surface under study. Moreover, in general ultra high vacuum, in the range of 10^{-7} pascal pressure or better, is necessary to reduce surface contamination by residual gas, by reducing the number of molecules reaching the sample over a given time period. At 0.1 mPa (10^{-6} Torr), it only takes 1 second to cover a surface with a contaminant, so much lower pressures are needed for measurements.

Purely optical techniques can be used to study interfaces under a wide variety of conditions. Reflection-absorption infrared, dual polarization interferometry, surface enhanced Raman, and some frequency generation spectroscopies can be used to probe solid-vacuum as well as solid-gas, solid-liquid, and liquid-gas surfaces. Modern physical analysis methods include scanning-tunneling microscopy (STM) and a family of methods descended from it. These microscopies have considerably increased the ability and the desire of surface scientists to measure the physical structure of many surfaces. This increase is related to a more general interest in nanotechnology.

6.6.4 Colloid Chemistry

Colloid chemistry is defined as the study of the properties of matter whose particles are colloidal in size in at least one dimension, usually those particles of matter are larger than ordinary molecules but smaller than objects that can be seen with an optical microscope.

A **colloid** is a substance microscopically dispersed evenly throughout another one, and a colloidal system consists of two separate phases: a *dispersed phase* (or internal phase) and a *continuous phase* (or dispersion medium). A colloidal system may be solid, liquid, or gaseous. Many familiar substances are colloids, such as fog, smoke, milk, blood and jelly. As well as these naturally occurring colloids, modern chemical process industries utilize high shear mixing technology to create novel colloids.

The dispersed-phase particles have a diameter of between approximately 5 and 200 nanometers. Such particles are normally invisible to an optical microscope, though their presence can be confirmed with the use of an ultramicroscope or an electron microscope. Homogeneous mixtures with a dispersed phase in this size range may be called colloidal *aerosols*, colloidal *emulsions*, colloidal *foams*, colloidal *dispersions*, or *hydrosols*. The dispersed-phase particles or droplets are affected largely by the surface chemistry present in the colloid. Some colloids are translucent because of the **Tyndall effect**, which is the scattering of light by particles in the colloid. Other colloids may be opaque or have a slight color.

Several forces play an important role in the interaction of colloid particles and affect the **stability of colloidal system**: electrostatic interaction, steric forces, excluded volume repulsion, van der Waals forces and entropic forces.

Stabilization of a colloidal dispersion serves to prevent colloids from aggregating. *Steric stabilization* and *electrostatic stabilization* are the two main mechanisms for colloid stabilization. Electrostatic stabilization is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, so that an electrical double layer forms at any interface. Small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its *buoyancy* or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase. The charge on the dispersed particles can be observed by applying an electric field: All particles migrate to the same electrode and therefore must all have the same sign charge.

Unstable colloidal dispersions form *flocs* as the particles aggregate due to interparticle attractions. In this way photonic glasses can be grown. This can be accomplished by a number of different methods: (1) Removal of the electrostatic barrier that prevents aggregation of the particles. (2) Addition of a charged polymer *flocculant*. (3) Addition of non-adsorbed polymers called *depletants* that cause aggregation due to entropic effects. (4) Physical deformation of the particle (e.g., stretching) may increase the van der Waals forces more than stabilization forces (such as electrostatic), resulting coagulation of colloids at certain orientations.

Unstable colloidal suspensions of low-volume fraction form clustered liquid *suspensions*, wherein individual clusters of particles fall to the bottom of the suspension (or float to the top if the particles are less dense than the suspending medium) once the clusters are of sufficient size for the *Brownian forces* that work to keep the particles in suspension to be overcome by gravitational forces. However, colloidal suspensions of higher-volume fraction form colloidal gels with *viscoelastic* properties. Viscoelastic colloidal gels, such as bentonite and toothpaste, flow like liquids under shear, but maintain their shape when shear is removed. It is for this reason that toothpaste can be squeezed from a toothpaste tube, but stays on the toothbrush after it is applied.

6.7 Crystal Structure

In mineralogy and crystallography, crystal structure is a unique arrangement of atoms or molecules in a crystalline liquid or solid. A crystal structure is composed of a pattern, a set of atoms arranged in a particular way, and a *lattice* exhibiting long-range order and symmetry. *Patterns* are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions. The points can be thought of as forming identical tiny boxes, called *unit cells*, that fill the space of the lattice. The lengths of the edges of a unit cell and the angles between them are called the *lattice parameters*. The symmetry properties of the crystal are embodied in its space group. A crystal's structure and symmetry play a role in determining many of its physical properties, such as cleavage, electronic band structure, and optical transparency.

6.7.1 Unit Cell

The crystal structure of a material or the arrangement of atoms within a given type of crystal structure can be described in terms of its unit cell. The **unit cell** is a tiny box containing one or more atoms, a spatial arrangement of atoms. The unit cells stacked in three-dimensional space describe the bulk arrangement of atoms of the crystal. The crystal structure has a three dimensional shape. The unit cell is given by its lattice parameters, the length of the cell edges and the angles between them, while the positions of the atoms inside the unit cell are described by the set of atomic positions (x_i, y_i, z_i) measured from a lattice point.

1. Miller Indices

Vectors and atomic planes in a crystal lattice can be described using a three-value *Miller index notation* (lmn). The l, m and n directional indices are separated by 90°, and are thus *orthogonal*. In fact, the l component is mutually perpendicular to the m and n indices.

By definition, (lmn) denotes a plane that intercepts the three points

a_1/l, a_2/m, and a_3/n, or some multiple thereof. That is, the Miller indices are proportional to the inverses of the intercepts of the plane with the unit cell (in the basis of the lattice vectors). If one or more of the indices is zero, it simply means that the planes do not intersect that axis (i.e. the intercept is "at infinity").

2. Planes and Directions

The crystallographic directions are fictitious lines linking nodes (atoms, ions or molecules) of a crystal. Similarly, the crystallographic planes are fictitious planes linking nodes. Some directions and planes have a higher density of nodes. These high density planes have an influence on the behavior of the crystal as follows:

(1) *Optical properties*: Refractive index is directly related to density (or periodic density fluctuations).

(2) *Adsorption and reactivity*: Physical adsorption and chemical reactions occur at or near surface atoms or molecules. These phenomena are thus sensitive to the density of nodes.

(3) *Surface tension*: The condensation of a material means that the atoms, ions or molecules are more stable if they are surrounded by other similar species. The surface tension of an interface thus varies according to the density on the surface.

(4) *Microstructural defects*: Pores and crystallites tend to have straight grain boundaries following higher density planes.

(5) *Cleavage*: This typically occurs preferentially parallel to higher density planes.

(6) *Plastic deformation*: Dislocation glide occurs preferentially parallel to higher density planes. The perturbation carried by the dislocation (*Burgers vector*) is along a dense direction. The shift of one node in a more dense direction requires a lesser distortion of the crystal lattice.

6.7.2 Classification

The defining property of a crystal is its *inherent symmetry*, by which we mean that under certain "operations" the crystal remains unchanged. For example, rotating the crystal 180° about a certain axis may result in an atomic configuration which is identical to the original configuration. The crystal is then said to have a *twofold rotational symmetry* about this axis. In addition to rotational symmetries like this, a crystal may have symmetries in the form of *mirror planes* and *translational symmetries*, and also the so-called "*compound symmetries*" which are a combination of translation and rotation/mirror symmetries. A full classification of a crystal is achieved when all of these inherent symmetries of the crystal are identified.

1. Lattice Systems

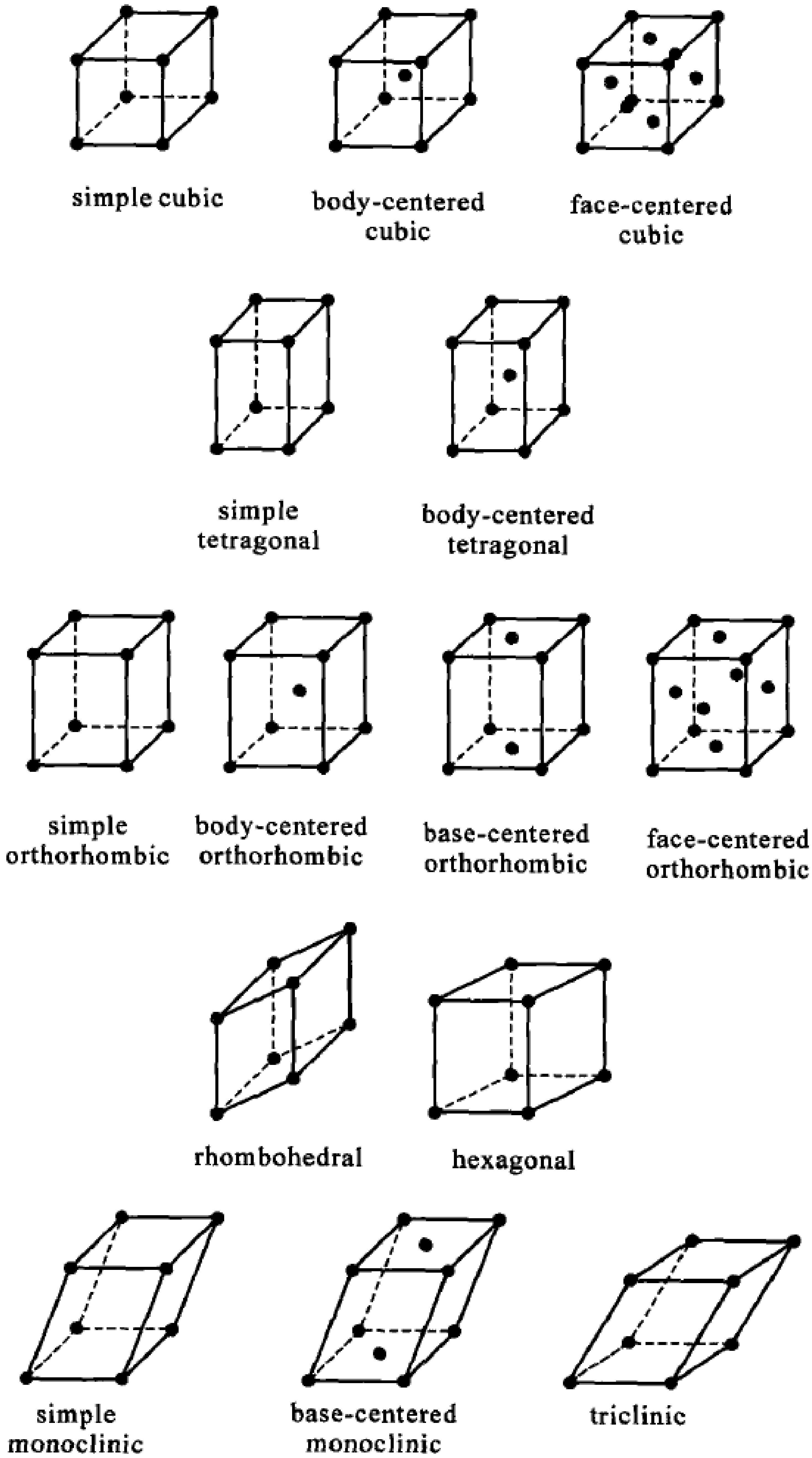
These lattice systems are a grouping of crystal structures according to the axial system used to describe their lattice. Each lattice system consists of a set of three axes in a particular geometrical arrangement. There are seven lattice systems. They are similar to but not quite the same as the seven crystal systems and the six crystal families.

The simplest and most symmetric, the *cubic* (or isometric) system, has the symmetry of a cube, that is, it exhibits four threefold rotational axes oriented at 109.5° (the tetrahedral angle) with respect to each other. These threefold axes lie along the body diagonals of the cube. The other six lattice systems, are *hexagonal*, *tetragonal*, *rhombohedral* (often confused with the trigonal crystal system), *orthorhombic*, *monoclinic* and *triclinic*.

2. Bravais Lattices

When the crystal systems are combined with the various possible lattice centerings, we arrive at the *Bravais lattices*. The Bravais lattices are sometimes referred to as *space lattices*. They describe the geometric arrangement of the lattice points, and thereby the translational symmetry of the crystal. In three dimensions, there are 14 unique Bravais lattices which are distinct from one another in the translational symmetry they contain. All crystalline materials recognized until now (not including *quasicrystals*) fit in one of these arrangements. The fourteen three-dimensional lattices, classified by crystal system, are shown in Figure 6.1.

The crystal structure consists of the same group of atoms, the basis, positioned around each and every lattice point. This group of atoms therefore repeats indefinitely in three dimensions according to the arrangement of one



simple cubic

body-centered cubic

face-centered cubic

simple tetragonal

body-centered tetragonal

simple orthorhombic

body-centered orthorhombic

base-centered orthorhombic

face-centered orthorhombic

rhombohedral

hexagonal

simple monoclinic

base-centered monoclinic

triclinic

Figure 6.1 Bravais lattices

of the 14 Bravais lattices. The characteristic rotation and mirror symmetries of the group of atoms, or unit cell, is described by its crystallographic point group.

3. Point Groups

The crystallographic **point group** or *crystal class* is the mathematical group comprising the symmetry operations that leave at least one point unmoved and that leave the appearance of the crystal structure unchanged. These symmetry operations include:

(1) *Reflection*, which reflects the structure across a reflection plane.

(2) *Rotation*, which rotates the structure a specified portion of a circle about a rotation axis.

(3) *Inversion*, which changes the sign of the coordinate of each point with respect to a center of symmetry or inversion point.

(4) *Improper rotation*, which consists of a rotation about an axis followed by an inversion.

Rotation axes (proper and improper), *reflection planes*, and *centers of symmetry* are collectively called *symmetry elements*. There are 32 possible crystal classes. Each one can be classified into one of the seven crystal systems.

4. Space Groups

The **space group** of the crystal structure is composed of the translational symmetry operations in addition to the operations of the point group. These include:

(1) *Pure translations*, which move a point along a vector.

(2) *Screw axes*, which rotate a point around an axis while translating parallel to the axis.

(3) *Glide planes*, which reflect a point through a plane while translating it parallel to the plane.

There are 230 distinct space groups.

References

[1] Atkins P W, Paula J D. Physical chemistry [M]. New York: W.H. Freeman, 2002.

[2] Levine I N. Physical chemistry: sixth edition [M]. New York: McGraw-Hill, 2008.

[3] McQuarrie D A, Simon J D. Physical chemistry [M]. Sausalito: University Science Books, 1997.

[4] Silbey R J, Alberty R A, Bawendi M G. Physical chemistry [M]. Hoboken: John Wiley & Sons, 2005.

[5] http://www.science.uwaterloo.ca.

[6] http://onsager.bd.psu.edu.

[7] http://en.wikipedia.org.

[8] http://che.cycu.edu.tw.

[9] http://www.answers.com.

[10] http://www.thefreedictionary.com.

[11] http://www.chemistryexplained.com.

[12] http://www.chem.ufl.edu.

[13] http://chemistry.about.com.

[14] http://www.chemguide.co.uk.

[15] http://library.thinkquest.org.

[16] http://www.engineeringtoolbox.com.

[17] http://www.wpi.edu.

[18] http://www.chem1.com.

[19] http://www.sciencedaily.com.

[20] http://cnx.org/content/m16927/latest/.

Chapter 7 Analytical Chemistry

7.1 Introduction

7.1.1 What is Analytical Chemistry

Analytical chemistry is the science of inventing and applying the concepts, principles, and strategies for measuring the characteristics of chemical systems and species. Analytical Chemistry is concerned with providing **qualitative** and **quantitative** information about the chemical and structural composition of a sample of matter. **Qualitative analysis** gives an indication of the identity of the chemical species in the sample and **quantitative analysis** determines the amount of one or more of these components. The **separation** of components is often performed prior to analysis.

A huge variety of samples, from high concentrations of elements in alloy steels to part-per-billion (ppb) levels of drugs in biological tissue, are handled by the analyst. The field is founded on the conversion of a measured physical property of the species being examined to a usable signal. Analytical methods are generally divided into two categories, classical and instrumental, on the basis of their historical development. **Classical methods** (also known as **wet chemistry methods**) use separations such as **precipitation**, **extraction**, and **distillation** and qualitative analysis by **color**, **odor**, or **melting point**. Quantitative analysis is achieved by measurement of **weight** or **volume**. **Instrumental methods** use an apparatus to measure physical quantities of the analyte such as **light absorption**, **fluorescence**, or **conductivity**. The separation of materials is accomplished using **chromatography** or **electrophoresis** methods. The overall strategy is to prepare a sample correctly, choose a particular method of analysis, and report the results in a meaningful format, which may include a statistical evaluation.

Analytical chemistry plays a vital role in the development of science and has evolved from an art into a science with applications in forensics, bioanalysis, clinical analysis, environmental analysis, and materials analysis, etc.

7.1.2 Stepping Through a Typical Quantitative Analysis

A typical quantitative analysis involves the following sequence of steps:

(1)Picking a Method.

(2)Acquiring the Sample. **Sampling** involves obtaining a small mass of a material whose composition accurately represents the bulk of the material being sampled. Whether sampling is simple or complex, however, the analyst must be sure that the laboratory sample is representative of the whole before proceeding with an analysis.

(3)Processing the Sample. Its first step is often the preparation of a laboratory sample. Replicate samples are defined to ensure the reliability of the measurement.

(4)Eliminating interferences. Species other than the analyte that affect the final measurement are called **interferences**, or **interferents**.

(5)Calibration and Measurement.

(6)Calculating Results.

(7)Evaluating Results by Estimating Their Reliability.

7.2 Chemicals and Apparatus

7.2.1 Grades of Chemicals

The purity of reagents has an important bearing on the accuracy that can be attained in any analysis. Chemical reagents are available in such varying degrees of purity, and the most common commercial grades of reagents are as follows:

Reagent Grade (*R. G.*) - Reagent-grade chemicals conform to the minimum standards set forth by the Reagent Chemical Committee of the American Chemical Society and are used wherever possible in analytical work.

Primary Standard Grade - Analytical reagent of exceptional purity that is specially manufactured for standardizing volumetric solutions and preparing reference standards.

Analytical Reagent (*A. R.*) *Grade* - If the reagent also meets the requirements of the American Chemical Society Committee on Analytical Reagent, it will be denoted as an A. R. (ACS) reagent.

Guaranteed Reagent (*G. R.*) *Grade* – It is the ideal quality for laboratory purposes. The grade is equivalent to Analytical grade (A. R.) and Reagent grade (R. G.).

Organic reagents (*O. R.*) *Grade* – Organic reagents that are suitable for research applications.

Chemically Pure (*C. P.*) *Grade*— Products of purity suitable for use in general applications.

Technical Grade — A grade suitable for non-critical tasks in the laboratory such as rinsing, dissolving or for general industrial use.

7.2.2 Apparatus

In most analyses, an *analytical balance* is used to measure mass to a very high degree of precision and accuracy. *Desiccators* are sealable enclosures containing *desiccants* used for preserving moisture-sensitive items. A common use for desiccators is to protect chemicals which are *hygroscopic* or which react with water from humidity. A *crucible* is a cup-shaped piece of laboratory equipment used to contain chemical compounds when heated to extremely high temperatures. Crucibles are available in several sizes and typically come with a correspondingly-sized crucible cover (or lid). *Beakers*, *dropping pipets*, and *graduated cylinders* are used to measure volumes approximately, typically with errors of several percent. The reliable measurement of volume is performed with a *pipet*, a *buret*, and a *volumetric flask*. A *pipet* (also called *pipette*) is used to transport an accurately known volume of liquid from one container to another. Numerous *automatic* pipets are available for situations that call for the repeated delivery of a particular volume. In addition, motorized, computer-controlled microliter pipets are now available. A *burette* (also *buret*) is a vertical cylindrical piece of laboratory glassware with a volumetric graduation on its full length and a precision *tap*, or *stopcock*, on the bottom. It is used to dispense known amounts of a liquid reagent in experiments for which such precision is necessary, such as a titration experiment. A *volumetric flask* is used to make up a solution of fixed volume very accurately.

7.3 Evaluating Analytical Data

It is impossible to perform a chemical analysis in such a way that the results are totally free of *errors* or *uncertainties*. We can only hope to minimize these errors and estimate their size with acceptable accuracy.

7.3.1 Definitions

Mean, or *arithmetic mean*, $\bar{X}$, is the numerical *average* obtained by dividing the sum of the individual measurements by the number of measurements

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where X_i is the i^{th} measurement, and n is the number of independent measurements. The arithmetic mean is used to report a best value among a series of n replicate measurements.

The *median*, X_{med}, is the middle value when data are ordered from the smallest to the largest value. For an odd number of measurements, the median is the middle value. For an even number of measurements, the median is the average of the middle pair measurements.

The terms *accuracy* and *precision* have been introduced in Chapter 1. Accuracy measures agreement between a result and its true value (X_t). Precision describes the agreement among several results that have been obtained in the same way. Accuracy is usually expressed as either an *absolute error*

$$E = \bar{X} - X_t$$

or a percent relative error, E_r.

$$E_r = \frac{\bar{X} - X_t}{X_t} \times 100\%$$

The *spread*, or *range*, w, is the difference between the largest and the smallest values in the data set.

$$\text{Range} = w = X_{\text{largest}} - X_{\text{smallest}}$$

Three terms are widely used to describe the precision of a set of replicate data: *standard deviation*, *variance*, and *coefficient of variation*. All these terms are a function of the *deviation from the mean* d_i, or just the *deviation*, which is defined as

$$d_i = |X_i - \bar{X}|$$

The *absolute standard deviation*, S, describes the spread of individual measurements about the mean and is given as

$$S = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1}}$$

Frequently, the *relative standard deviation*, S_r, is reported. $S_r = \frac{S}{\bar{X}}$

The *percent relative standard deviation* is obtained by multiplying S_r by 100%.

Errors affecting the accuracy of an analysis are called *systematic* (or *determinate*) and are characterized by a systematic deviation from the true value. Determinate errors may be divided into four categories: *sampling errors*, *method errors*, *measurement errors*, and *personal errors*.

Errors affecting the precision of an analysis are called *random* (or *indeterminate*) errors. This type of error is caused by the many uncontrollable variables.

Analytical chemists make a distinction between *error* and *uncertainty*. Error is the difference between a single measurement or result and its *true value*. In other words, error is a measure of *bias*. *Uncertainty* expresses the range of possible values that a measurement or result might reasonably be expected to have. Uncertainty accounts for all errors, both determinate and indeterminate, that might affect our result.

7.3.2 The Distribution of Measurements and Results

In statistics, a finite number of experimental observations is called a *sample* of data. A *population* is a collection of data whose properties are analyzed. The population is the complete collection to be studied, it contains all subjects of interest. A sample is a part of the population of interest, a subcollection selected from a population.

The distribution of a population can be represented by plotting the frequency of occurrence of individual values as a function of the values themselves. Such plots are called *probability distributions*. The most commonly encountered continuous distribution is the *Gaussian*, or *normal distribution*, where the frequency of occurrence for a value, X, is given by

$$f(X) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[\frac{-(X-\mu)^2}{2\sigma^2}\right]$$

The shape of a normal distribution is determined by two parameters, the first of which is the *population's central*, or *true mean value*, μ, give as

$$\mu = \frac{\sum_{i=1}^{N} X_i}{N}$$

where N is the size of the population. The second parameter is the population's *variance*, σ^2, which is calculated using the following equation

$$\sigma^2 = \frac{\sum_{i=1}^{N} (X_i - \mu)^2}{N}$$

σ is the *population standard deviation*, which is a measure of the precision or scatter of a population of data.

A *confidence interval* gives an estimated range of values which is likely to include an unknown population parameter, the estimated range being calculated from a given set of sample data. A confidence interval is always qualified by a particular *confidence level*, usually expressed as a percentage; thus one speaks of a "95% confidence interval". The end points of the confidence interval are referred to as *confidence limits*.

7.3.3 Statistical Analysis of Data

A statistical analysis allows us to determine whether our results are significantly different from known values, or from values obtained by other analysts, by other methods of analysis, or for other samples. A ***t*-test** is used to compare mean values, and an ***F*-test** to compare precisions. Comparisons between two sets of data require an initial evaluation of whether the data is *paired* or *unpaired*. For unpaired data it is also necessary to decide if the standard deviations can be pooled. A decision about whether to retain an *outlying value* can be made using Dixon's ***Q*-test**. The **detection limit** is a statistical statement about the smallest amount of analyte that can be detected with confidence. A detection limit is not exact because its value depends on how willing we are to falsely report the analyte's presence or absence in a sample. When reporting a detection limit, you should clearly indicate how you arrived at its value.

7.4 Gravimetric Methods of Analysis

Gravimetry is one of the oldest techniques of quantitative analysis. **Gravimetric analysis** describes a set of methods in analytical chemistry for the quantitative determination of an analyte based on the *mass* of a solid. The steps commonly followed in gravimetric analysis are (1)preparation of a solution containing a known weight of the sample, (2)separation of the desired constituent, (3)weighing the isolated constituent, and (4)computation of the amount of the particular constituent in the sample from the observed weight of the isolated substance. There are two major types of gravimetric methods: **precipitation methods** and **volatilization methods**.

7.4.1 Precipitation Methods

In **precipitation methods**, the analyte must first be converted to a solid by precipitation with an appropriate reagent. After collecting and drying, the precipitate is weighed on an analytical balance and the amount of analyte in the original sample can then be calculated from the mass of the precipitate and its chemical composition.

For example, the Association of Official Analytical Chemists recommends a precipitation method for determining calcium in natural waters. In this method, an excess of oxalic acid, $H_2C_2O_4$, is added to a carefully measured volume of the sample. Ammonia is then added to neutralize the solution and cause the calcium in the sample to precipitate as calcium oxalate. The reactions are

$$2NH_3 + H_2C_2O_4 \rightarrow 2NH_4^+ + C_2O_4^{2-}$$

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)$$

The precipitate is filtered using a weighed filtering crucible and is dried and ignited. This process converts the precipitate entirely to calcium oxide. The reaction is

$$CaC_2O_4(s) \rightarrow CaO(s) + CO(g) + CO_2(g)$$

After cooling, the crucible and precipitate are weighed and the mass of calcium oxide is determined by subtraction of the known mass of the crucible. The calcium content of the sample is then computed.

7.4.2 Volatilization Methods

In **volatilization methods**, the analyte or its decomposition products are volatilized at a suitable temperature. The volatile product is then collected and weighed, or, alternatively, the mass of the loss in mass of the sample. An example of a gravimetric volatilization procedure is the determination of carbonate in a mineral analysis. The sample is treated with an acid, and carbon dioxide is evolved as a gas. The gas is absorbed on a weighed quantity of a solid alkaline reagent.

All gravimetric methods are subject to some degree of error. The sensitivity and accuracy of gravimetric analyses are limited by the analytical balance used for measurements. However, other factors must also be considered, such as solubility losses, coprecipitation errors, and mechanical losses of the precipitate.

Gravimetric methods are the method of choice, particularly if the analyte concentration in the sample is larger that 1%. Other analytical methods should be considered for analyte concentrations less than 0.1%.

Reagents used for gravimetric methods tend to form precipitates with groups of ions. In this sense they are selective. Usually they do not form precipitates with a specific ion. This means that ions within a group interfere with the determination of any other ion in the group unless a preliminary separation is performed.

7.5 Titrimetric Methods of Analysis

Titrimetric methods include a large and powerful group of quantitative procedures based on measuring the amount of a reagent of known concentration that is consumed by an analyte. Because volume measurements play a key role in titration, it is also known as **volumetric analysis**. Titrimetric methods are widely used for routine determinations because they are rapid, convenient, accurate, and readily automated.

7.5.1 Overview of Titrimetry

A **primary standard** is a highly purified compound that serves as a reference material in all volumetric and mass titrimetric methods. The accuracy of a method is critically dependent on the properties of this compound. Compounds that meet or even approach these criteria are very few, and only a limited number of primary standard substances are available to the chemist. As a consequence, less pure compounds must sometimes be used in lieu of a primary standard. The purity of such a *secondary standard* must be established by careful analysis.

A **standard solution** (or a standard titrant) is a reagent of known concentration that is used to carry out a titrimetric analysis. The accuracy of a titrimetric method can be no better than the accuracy of the concentration of the standard solution used in the titration. Two basic methods are used to establish the concentration of such solutions. The first is the *direct method* in which a carefully weighed quantity of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask. The second is by *standardization* in which the titrant to be standardized is used to titrate (1)a weighed quantity of a primary standard, (2)a weighed quantity of a secondary standard, or (3)a measured volume of another standard solution. A titrant that is standardized against a secondary standard or against another standard solution is sometimes referred to as a *secondary standard solution*.

A **titration** is performed by adding a standard solution from a buret or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete. The volume of reagent needed to complete the titration is determined from the difference between the initial and final volume readings.

The **equivalence point** in a titration is reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample. For example, the equivalence point in the titration of sodium chloride with silver nitrate occurs after exactly 1 mol of silver ion has been added for each mole of chloride ion in the sample. The equivalence point in the titration of sulfuric acid with sodium hydroxide is reached after introduction of 2 mol of base for each mole of acid.

The term **back titration** is used when a titration is done "backwards"; instead of titrating the original analyte, one adds a known excess of a standard reagent to the solution, then titrates the excess. A back titration is useful if the endpoint of the reverse titration is easier to identify than the endpoint of the normal titration. They are also useful if the reaction between the analyte and the titrant is very slow.

The equivalence point of a titration cannot be determined experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of equivalence. This change is called the **end point** for the titration. Every effort is made to ensure that any volume or mass difference between the equivalence point and the end point is small. Such differences do exist, however, as a result of inadequacies in the physical changes and in our ability to observe them. The difference in volume or mass between the equivalence point and the end point is the **titration error**.

Indicators are often added to the analyte solution to give an observable physical change (the end point) at or near the equivalence point. We shall see that large changes in the relative concentration of analyte or titrant occur in the equivalence-point region. These concentration changes cause the indicator to change in appearance. Typical indicator changes include the appearance or disappearance of a color, a change in color, or the appearance or disappearance of turbidity.

We often use instruments to detect end points. These instruments respond to certain properties of the solution that change in a characteristic way during the titration. Instruments for detecting end points include colorimeters, turbidimeters, temperature monitors, voltmeters, current meters, and conductivity meters.

A **titration curve** is a curve in the plane whose x-coordinate is the volume of titrant added since the beginning of the titration, and whose y-coordinate is the concentration of the analyte at the corresponding stage of the titration (in an acid-base titration, the y-coordinate is usually the pH of the solution at the corresponding stage). In the case of acid-base titrations, titration curves reflect the strength of the corresponding acid and base. For instance, in a strong acid and strong base titration, the titration curve will be relatively smooth, although very steep for points near the equivalence point of the titration. Since in this case, small changes in the volume of the titrant result in large changes of the pH near the equivalence point, an extensive range of indicators would be appropriate (for instance *litmus*, *phenolphthalein* or *bromothymol blue*).

7.5.2 Types of Titrations

Titrimetric methods can be classified into four groups based on the type of reaction involved. These groups are **acid-base titrations**, which are based on the neutralization reaction that occurs between an acid and a base; **complexometric titrations** involving a metal-ligand complexation reaction which is used for the determination of a multitude of different cations; **redox titrations**, in which the analyte is consumed by an oxidizing or a reducing reagent of known concentration; and **precipitation titrations**, in which the analyte and titrant react to form a precipitate of limited solubility.

7.6 Electrochemical Methods of Analysis

At present, electrochemical methods of analysis are usually used to solve ecoanalytical, medical, and biological problems, and also the problems of diagnostics and certification of materials and items made of them. The merits of these methods are relative ease in handling the corresponding equipment, low cost of analysis, high sensitivity, sufficient selectivity and rapidity of determination, and the possibilities for the automatic control over the measurements of the analytical signal.

Electroanalytical methods are based on electrochemical phenomena occurring within a medium or at the phase boundary and related to changes in the structure, chemical composition, or concentration of the compound being analyzed. These methods are divided into five major groups: *potentiometry*, *voltammetry*, *coulometry*, *conductometry*, and *dielectrometry*.

7.6.1 Potentiometry

Analytical methods that are based on potential measurements are called **potentiometric methods**, or **potentiometry**. Potentiometry passively measures the potential of a solution between two electrodes under static conditions, affecting the solution very little in the process. The potential is then related to the concentration of one or more analytes. Potentiometric measurements are made using a **potentiometer** to determine the difference in potential between a *working* or, *indicator*, electrode and a *counter* or, *reference*, electrode.

A typical cell for potentiometric analysis can be depicted as

$$\underbrace{\text{reference electrode}}_{E_{ref}} \mid \underbrace{\text{salt bridge}}_{E_j} \mid \underbrace{\text{analyte solution} \mid \text{indicator electrode}}_{E_{ind}}$$

The *reference electrode* is a half-cell with an accurately known electrode potential, E_{ref}, that is independent of the concentration of the analyte or any other ions in the solution under study. The *indicator electrode*, which is immersed in a solution of the analyte, develops a potent potential, E_{ind}, that depends on the activity of the analyte. The net *junction potential* across the salt bridge, E_j, is small enough to be neglected for most electroanalytical method.

Potentiometry usually uses electrodes made selectively sensitive to the ion of interest, such as a fluoride-selective electrode. The most common potentiometric electrode is the glass-membrane electrode used in a pH meter.

7.6.2 Coulometry

Coulometric methods are performed by measuring the quantity of electrical charge (electrons) required to completely convert an analyte from one oxidation state to another. There are two forms of coulometry: *controlled-potential coulometry*, or *potentiostatic coulometry*, in which a constant potential is applied to the electrochemical cell, and *controlled-current coulometry*, or *amperostatic coulometry*, in which a constant current is passed through the electrochemical cell. The latter includes both direct and indirect methods, *electroanalysis*, and *coulometric titration*.

The instrumentation for potentiostatic coulometry consists of an electrolysis cell, a *potentiostat*, and a device for determining the number of coulombs (*coulometer*) consumed by the analyte. Controlled-current coulometry normally is carried out using a *galvanostat* (or *amperostat*), and an electrochemical cell consisting of a working electrode and a counter electrode.

In these experiments, the total current passed is measured directly or indirectly to determine the number of electrons(*coulombs*) passed. Knowing the number of electrons passed can indicate the concentration of the analyte or, when the concentration is known, the number of electrons transferred in the redox reaction.

7.6.3 Voltammetry

Voltammetry is based on the study of the dependence of polarization current on the voltage applied to an electrochemical cell when the potential of the working electrode differs significantly from the equilibrium value. In voltammetry a time-dependent potential is applied to an electrochemical cell, and the current flowing through the cell is measured as a function of that potential. A plot of current as a function of applied potential is called a **voltammogram**, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction. This method can reveal the reduction potential of an analyte and its electrochemical reactivity.

Modern voltammetry makes use of a three-electrode potentiostat. A time-dependent potential excitation signal is applied to the *working electrode*, changing its potential relative to the fixed potential of the *reference electrode*. The resulting current between the working and *auxiliary electrodes* is measured. The auxiliary electrode is generally a platinum wire, and the *saturated calomel electrode* (SCE) and Ag/AgCl electrode are common reference electrodes.

There are several important electroanalytical methods. In the simplest voltammetric methods, the potential of the working electrode is linearly increased or decreased. *Linear-scan voltammetry* is of two types: *hydrodynamic* *voltammetry* and *polarography*.

The earliest voltammetric technique, **polarography**, was developed by Czechoslovakian chemist Jaroslav Heyrovsky (1890—1967) in the early 1920s, for which he was awarded the Nobel Prize in chemistry in 1959. Polarometry uses a *dropping mercury electrode* (DME) as the working microelectrode. The auxiliary electrode is often the resulting mercury pool. In polarography a *limiting current* is obtained because each falling drop of mercury returns the solution near the electrode to its initial composition.

In **hydrodynamic voltammetry** current is measured as a function of the potential applied to a solid working electrode. Because hydrodynamic voltammetry is not limited to Hg electrodes, it is useful for the analysis of analytes that are reduced or oxidized at more positive potentials.

Amperometry is a form of voltammetry in which we measure current as a function of time while maintaining a constant potential.

Stripping voltammetry is a form of voltammetry in which the analyte is first deposited on the electrode and then removed, or "stripped", electrochemically while monitoring the current as a function of the applied potential. It is composed of three related techniques: *anodic*, *cathodic*, and *adsorptive* stripping voltammetry.

Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. It can be used to determine diffusion coefficients and half cell reduction potentials.

7.6.4 Conductometry

Conductometry encompasses methods in which the electrical conductivity of electrolytes (aqueous and nonaqueous solutions, colloid systems, melts, and solids) is measured. It is based on the change in the concentration of a compound or the chemical composition of a medium in the interelectrode space; it is not linked with the electrode potential, which is usually close to the equilibrium value. Conductometry includes both *direct* analytical methods and *indirect* analytical methods using either *direct* or *alternating current* (low or high frequency current). It also includes *chrono-conductometry* and low-frequency and high-frequency titration.

7.6.5 Dielectrometry

Dielectrometry combines analytical methods based on the measurement of the dielectric constant of a substance resulting from the orientation of particles (molecules or ions) that have a dipole moment in an electric field. These methods are used to monitor the purity of dielectrics, for example, to detect small amounts of moisture. Dielectrometric titration is used to analyze solutions.

7.7 Spectroscopic Methods of Analysis

Spectroscopy is the use of the *absorption*, *emission*, or *scattering* of electromagnetic radiation by matter to qualitatively or quantitatively study the matter or to study physical processes. The matter can be atoms, molecules, atomic or molecular ions, or solids. The regions of the electromagnetic spectrum involved in the spectroscopic measurements include γ-ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio frequency (RF). The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. Spectroscopic analytical methods are based on measuring the radiant energy absorbed or emitted by a substance at characteristic wavelengths of the electromagnetic spectrum on excitation by an external energy source. Table 7.1 lists the representative spectroscopies involving the absorption and emission of energy. However, spectroscopy also includes the study of particles (e.g. electrons, ions) that have been sorted or otherwise differentiated into a spectrum as a function of some property (such as energy or mass).

Table 7.1 Representative Spectroscopies Involving Absorption and Emission of Energy

Type of Energy Transfer	Region of the Electromagnetic Spectrum	Spectroscopic Technique
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	UV/Vis spectroscopy
		atomic absorption spectroscopy
	infrared	infrared spectroscopy
	microwave	microwave spectroscopy
		electron spin resonance spectroscopy
	radio waves	nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	atomic emission spectroscopy
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	fluorescence spectroscopy
		phosphorescence spectroscopy
		atomic fluorescence spectroscopy

7.7.1 UV-Visible Spectroscopy

A diagram of the components of a typical UV - Visible **spectrometer** is shown in Figure 7.1. A beam of light from a visible and/or UV light source is separated into its component wavelengths by a *prism* or *diffraction grating*. Each *monochromatic* (single wavelength) beam in turn is split into two equal intensity beams by a *half-mirrored* device. One beam, the *sample beam*, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the *reference*, passes through an identical cuvette containing only the solvent. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

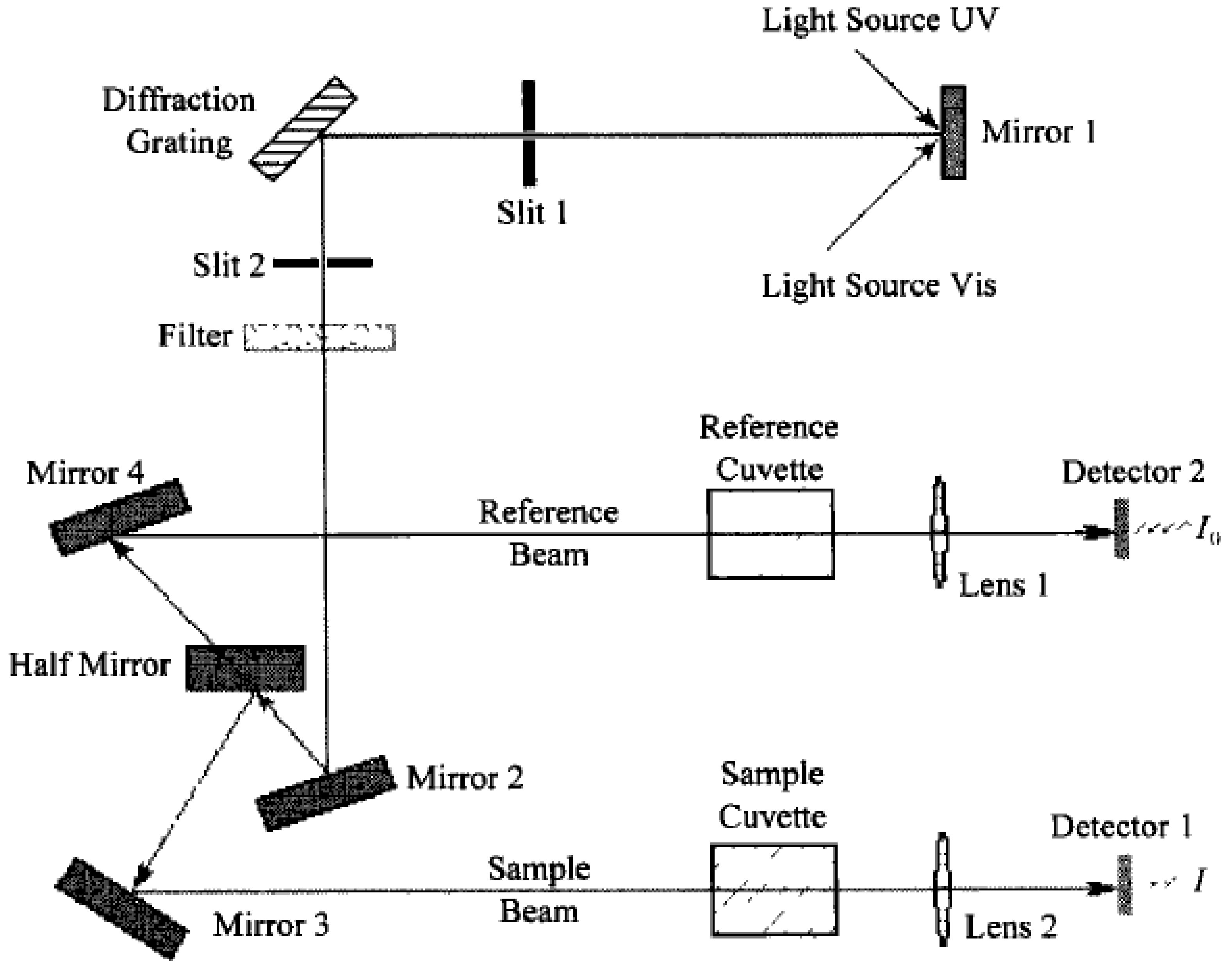


Figure 7.1 The diagram of the components of a typical UV—Visible spectrometer

Ultraviolet-visible(UV – Vis) spectroscopy corresponds to *electronic excitations* between the energy levels that correspond to the molecular orbitals of the systems. In particular, transitions involving π orbitals and lone pairs (n = non-bonding) are important and so UV – Vis spectroscopy is of most use for identifying conjugated systems which tend to have stronger absorptions.

For most molecules, the lowest energy occupied molecular orbitals are the σ-orbitals, those which correspond to σ-bonds. The π orbitals lie at somewhat higher energy levels, and those orbitals which hold unshared electron pairs, the non-bonding or n-orbitals, lie at even higher energies. The unoccupied or anti-bonding orbitals (π^* and σ^*) are the orbitals of highest energy. A typical progression of electronic energy levels is illustrated in Figure 7.2.

In all compounds other than alkanes, the electrons may undergo several possible transitions of different energies. Some of the most important transitions are:

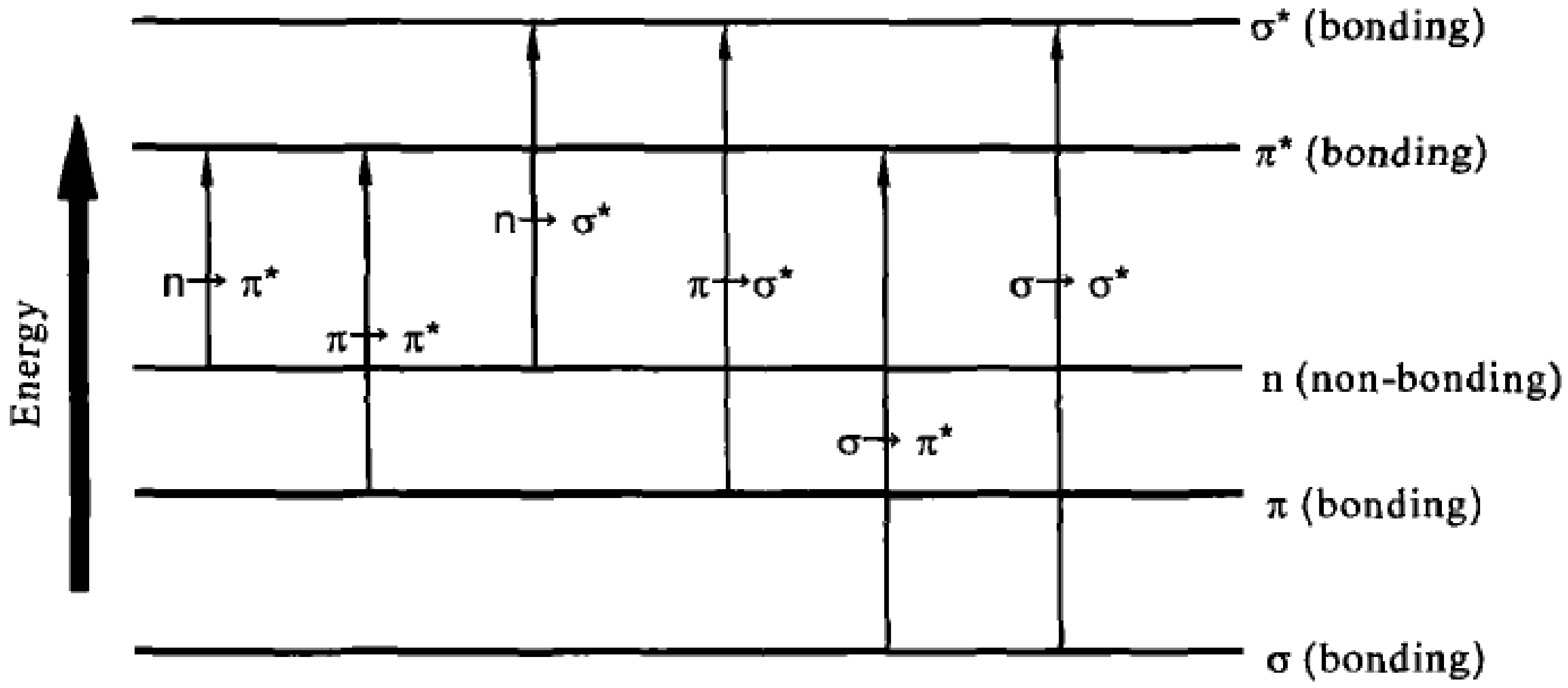


Figure 7.2 Electronic Energy Levels and Transitions

Increasing Energy ↓

$n\rightarrow\pi^*$ in carbonyl compounds

$n\rightarrow\sigma^*$ in oxygen, nitrogen, sulfur, and halogen compounds

$\pi\rightarrow\pi^*$ in alkenes, carbonyl compounds, alkynes, azo compounds, etc.

$\sigma\rightarrow\pi^*$ in carbonyl compounds

$\sigma\rightarrow\sigma^*$ in alkanes

A **$\sigma\rightarrow\sigma^*$ transition** requires quite high-energy radiation. In the usual case, $\sigma\rightarrow\sigma^*$ transitions are observed only in the region below 200 nm. For example, methane (which has only C－H bonds, and can only undergo $\sigma\rightarrow\sigma^*$ transitions) shows an absorbance maximum at 125 nm.

Saturated compounds containing atoms with lone pairs are capable of **$n\rightarrow\sigma^*$ transitions**. These transitions usually need less energy than $\sigma\rightarrow\sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150～250 nm.

Most applications of absorption spectroscopy to organic compounds are based on $n\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ transitions, because the energies required for these processes are such that the absorption bands for many compounds lie at wavelengths greater than 200 nm. Both types of transitions require the presence of an unsaturated site in the molecule to provide the π^* orbitals.

Molar absorbtivities from $n\rightarrow\pi^*$ transitions are relatively low, and range from 10 to 100 $L\cdot mol^{-1}\cdot cm^{-1}$. $\pi\rightarrow\pi^*$ transitions normally give molar absorbtivities between 1,000 and 10,000 $L\cdot mol^{-1}\cdot cm^{-1}$. Another characteristic difference of the two types of transitions occurs in the effect of solvent polarity on the wavelength of the bands. Peaks resulting from $n \rightarrow \pi^*$ transitions are generally shifted to shorter wavelengths (*hypsochromic* or *blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Usually, but not always, a reverse trend (*bathochromic* or *red shift*) is observed for $\pi \rightarrow \pi^*$ transitions. This is caused by attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and the unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and the unexcited states is slightly reduced, resulting in a small red shift. This effect also influences $\pi \rightarrow \pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

UV - Vis spectroscopy is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the **Beer-Lambert law**:

$$A = -\log T = -\log\left(\frac{I}{I_0}\right) = \varepsilon c l$$

where A is the measured *absorbance*, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, T is the *transmittance* which is defined as the ratio $\frac{I}{I_0}$ and is usually expressed as a percentage ($T\%$), l the length of sample cell (cm), and c the molar concentration of the absorbing species. For each species and wavelength, ε is a constant known as the *molar absorptivity* (formerly known as *molar extinction coefficient*).

7.7.2 IR Spectroscopy

Infrared spectroscopy (IR spectroscopy) deals with the interaction between a molecule and radiation from the IR region of the electromagnetic spectrum. It covers a range of techniques, the most common being a form of absorption spectroscopy. It can be used to identify compounds and investigate sample composition. A common laboratory instrument that uses this technique is an **infrared spectrophotometer**.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the *near-*, *mid-* and *far-* infrared, named for their relation to the visible spectrum. The *far-infrared*, approximately $400\sim10\ \text{cm}^{-1}$ ($25\sim1000\ \mu\text{m}$) has low energy and may be used for *rotational* spectroscopy. The *mid-infrared*, approximately $4000\sim400\ \text{cm}^{-1}$ ($2.5\sim25\ \mu\text{m}$) may be used to study the fundamental vibrations and associated *rotational-vibrational* structure. The higher energy *near-IR*, approximately $14000\sim4000\ \text{cm}^{-1}$ ($0.8\sim2.5\ \mu\text{m}$) can excite *overtone* or *harmonic vibrations*. The most useful IR region lies between $4000\sim670\ \text{cm}^{-1}$.

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are *resonant frequencies*, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The resonant frequencies can be related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

For a molecule to absorb IR, the vibrations or the rotations within a molecule must cause a net change in the dipole moment of the molecule. A molecule can vibrate in many ways, and each way is called a **vibrational mode**. Linear molecules have $3N-5$ degrees of vibrational modes (also called *vibrational degrees of freedom*) whereas nonlinear molecules have $3N-6$ degrees of vibrational modes. As an example H_2O, a non-linear molecule, will have $3\times3-6=3$ degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N_2, the band is not observed in the IR spectrum, but only in the Raman spectrum. Unsymmetrical diatomic molecules, e.g. CO, absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

Vibrations fall into the two main categories of *stretching* and *bending*. Stretching is the change in inter-atomic distance along bond axis. Bending is the change in angle between two bonds. There are four types of bend: *scissoring*, *rocking*, *wagging* and *twisting*. The atoms in a $-CH_2-$ group, commonly found in organic compounds, can vibrate in six different ways: *symmetric* and *antisymmetric stretching*, *scissoring*, *rocking*, *wagging* and *twisting*.

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a *monochromatic* beam, which changes in wavelength over time, or by using a **Fourier transform** instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

In general terms it is convenient to split an IR spectrum into two approximate regions: *functional group region* ($4000 \sim 1000\ \text{cm}^{-1}$) and *fingerprint region* ($< 1000\ \text{cm}^{-1}$). The most useful information obtained from an IR spectrum is what functional groups are present within the molecule.

Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an *interferometer* and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "*interferogram*", represents light output as a function of mirror position. A data-processing technique called *Fourier transform* turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength (or wavenumber).

7.7.3 Atomic Spectroscopy

Atomic spectroscopy is used for the qualitative and the quantitative determination of over 70 different metals. The methods can be based on *absorption*, *emission*, or *fluorescence*. **Atomic absorption spectroscopy** (**AAS**) currently is the most widely used of these techniques.

AAS is based on the absorption of element-specific primary source radiation by analyte atoms. In **AA spectroscopy**, as in all atomic spectroscopic methods, the sample must be converted into an atomic vapor by a process known as **atomization**. Several methods are used to atomize samples. The two most important of these for AA spectroscopy are *flame* and *furnace* (or *elec-*

trothermal) atomization. The electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity.

As the quantity of energy (the power) put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured, it is possible, from Beer-Lambert law, to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured.

In **atomic emission**, a sample is subjected to a high energy, thermal environment in order to produce excited atoms, which then emit characteristic radiation as they return to the ground state. The energy source can be an electrical arc, a flame, or more recently, an *inductively coupled plasma* (*ICP*). The emission spectrum of an element exposed to such an energy source consists of a collection of the allowable emission wavelengths, commonly called *emission lines*, because of the discrete nature of the emitted wavelengths. This emission spectrum can be used as a unique characteristic for qualitative identification of the element. Emission techniques can also be used for quantitative analysis to determine how much of an element is present in a sample. The technique of **flame photometry** is an application of atomic emission for quantitative analysis.

The third field of atomic spectroscopy is **atomic fluorescence**. This technique incorporates aspects of both atomic absorption and atomic emission. Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light into the atomic vapor. Instead of looking at the amount of light absorbed in the process, however, the emission resulting from the decay of the atoms excited by the source light is measured. The intensity of this "fluorescence" increases with increasing atom concentration, providing the basis for quantitative determination. The source lamp for atomic fluorescence is mounted at an angle to the rest of the optical system, so that the light detector sees only the fluorescence in the flame and not the light from the lamp itself. It is advantageous to maximize lamp intensity since sensitivity is directly related to the number of excited atoms which in turn is a function of the intensity of the exciting radiation.

7.7.4 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) is a property that magnetic nuclei have in a magnetic field and applied electromagnetic (EM) pulse or pulses, which cause the nuclei to absorb energy from the EM pulse and radiate this energy back out. **Nuclear magnetic resonance spectroscopy**, most commonly known as **NMR spectroscopy**, is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter.

All stable isotopes that contain an odd number of protons and/or of neutrons have an *intrinsic magnetic moment* and *angular momentum*, in other words a *nonzero spin*, while all nuclides with even numbers of both have spin 0. The most commonly studied nuclei are ^{1}H and ^{13}C, although nuclei from isotopes of many other elements (e.g. ^{11}B, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}Cl) are studied by high-field NMR spectroscopy as well.

When placed in a magnetic field, NMR active nuclei (such as ^{1}H or ^{13}C) absorb at a frequency characteristic of the isotope. The *resonant frequency*, energy of the absorption and the intensity of the signal are proportional to the strength of the magnetic field. For example, in a 21 tesla (T) magnetic field, protons resonate at 900 MHz. It is common to refer to a 21 T magnet as a 900 MHz magnet, although different nuclei resonate at a different frequency at this field strength.

The magnetic field at the nucleus is not equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the **nuclear shielding**. Depending on the local chemical environment, different protons in a molecule resonate at slightly different frequencies. Since both this frequency shift and the fundamental resonant frequency are directly proportional to the strength of the magnetic field, the shift is converted into a field-independent dimensionless value known as **the chemical shift**. The chemical shift is reported as a relative measure from some reference resonance frequency[For the nuclei ^1H, ^{13}C, and ^{29}Si, *TMS* (*tetramethylsilane*) is commonly used as a reference]. This difference between the frequency of the signal and the frequency of the reference is divided by frequency of the reference signal to give the chemical shift. The frequency shifts are extremely small in comparison to the fundamental NMR frequency. A typical frequency shift might be 100 Hz, compared to a fundamental NMR frequency of 100 MHz, so the chemical shift is generally expressed in parts per million (ppm), and designated by the symbol **δ**. The chemical shift is a very precise metric of the chemical environment around a nucleus.

Some of the most useful information for structure determination in a one-dimensional NMR spectrum comes from **J-coupling** or *scalar coupling* (a special case of *spin-spin coupling*) between NMR active nuclei. This coupling arises from the interaction of different spin states through the chemical bonds of a molecule and results in the *splitting* of NMR signals. These splitting patterns can be complex or simple, and likewise, can be straightforwardly interpretable or deceptive. This coupling provides detailed insight into the connectivity of atoms in a molecule.

Coupling to n equivalent (spin $\frac{1}{2}$) nuclei splits the signal into a $n+1$ multiplet with intensity ratios following *Pascal's triangle*. Coupling to additional spins will lead to further splittings of each component of the multiplet e.g. coupling to two different spin $\frac{1}{2}$ nuclei with significantly different coupling constants will lead to a *doublet of doublets* (abbreviation: dd). For example, in the ^1H NMR spectrum of ethanol, the methyl (CH_3) peak has been split into three peaks (a *triplet*) with an intensity ratio of 1 : 2 : 1 by the two neighboring methylene (CH_2) protons, similarly, the CH_2 peak has been split into four peaks (a *quartet*) with an intensity ratio of 1 : 3 : 3 : 1 by the three neighboring CH_3 protons. In principle, the two CH_2 protons would also be split again into a doublet to form a *doublet of quartets* by the hydroxyl proton, but intermolecular exchange of the acidic hydroxyl proton often results in a loss of coupling information.

NMR spectroscopy is routinely used by chemists to study chemical structure using simple *one-dimensional techniques*. *Two-dimensional techniques* are used to determine the structure of more complicated molecules. These techniques are replacing X-ray crystallography for the determination of protein structure. *Time domain NMR spectroscopic techniques* are used to probe molecular dynamics in solutions. *Solid state NMR spectroscopy* is used to determine the molecular structure of solids.

7.7.5 Mass Spectrometry

Mass spectrometry(MS) is an analytical technique that measures the *mass-to-charge ratio* of charged particles. It is used for determining masses of particles, for the determination of the elemental composition of a sample or molecule, and for elucidating the chemical structures of molecules. The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios.

When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** ($M^{+\cdot}$). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces ($F^{\cdot}$) and smaller **fragment ions** ($M^{+\cdot}$ and M^{+}). The molecular ion is a radical cation, but the fragment ions may either be radical cations ($M^{+\cdot}$) or carbocations (M^{+}), depending on the nature of the neutral fragment.

A **mass spectrum** will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio $\left(\frac{m}{z}\right)$ and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**.

In general a **mass spectrometer** consists of three modules: an *ion source*, in which a small sample of compound is ionized, usually to cations by loss of an electron; a *mass analyzer*, in which the ions are sorted and separated according to their mass and charge by applying electromagnetic fields; and an *ion detector*, which measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present. Since mass spectrometers create and manipulate gas-phase ions, they operate in a high-vacuum system.

Techniques for ionization have been key to determining what types of samples can be analyzed by mass spectrometry. **Electron impact** (EI) and **chemical ionization** (CI) are used for gases and vapors. In chemical ionization sources, the analyte is ionized by chemical ion-molecule reactions during collisions in the source. Two techniques often used with liquid and solid biological samples include *electrospray ionization* (ESI) and *matrix-assisted laser desorption/ionization* (MALDI). *Inductively coupled plasma* (ICP) sources are used primarily for cation analysis of a wide array of sample types.

There are many types of mass analyzers, using either static or dynamic fields, and magnetic or electric fields. *Sector field mass analyzer*, *time-of-flight* (TOF) *analyzer* and *quadrupole mass analyzer* are the most commonly used. Each analyzer type has its strengths and weaknesses. Many mass spectrometers use two or more mass analyzers for *tandem mass spectrometry* (MS/MS). In addition to the more common mass analyzers listed above, there are others designed for special situations.

7.8 Chromatographic and Electrophoretic Methods

Chromatography and **electrophoresis** are powerful analytical techniques that can separate a sample into its components while providing a means for determining their concentration.

7.8.1 Chromatography Terms

Chromatography (from Greek chroma "color" and graphein "to write") is the collective term for a set of laboratory techniques for the separation of mixtures. It involves passing a mixture dissolved in a *mobile phase* through a stationary phase, which separates the analyte to be measured from other molecules in the mixture based on *differential partitioning* between the mobile and the *stationary phases*. Subtle differences in a compound's *partition coefficient* result in differential *retention* on the stationary phase and thus changing the separation.

The *stationary phase* in chromatography is the extracting phase that remains in a fixed position. The *mobile phase* in chromatograph is a phase that moves over or through the stationary phase, carrying with it the analyte mixture. The mobile phase may be a gas, a liquid, or a supercritical fluid.

Elution is a process in which solutes are washed through a stationary phase by the movement of a mobile phase. The mobile phase that exits the column is called the *eluate*. The *eluent* is the solvent that will carry the analyte. An *eluotropic series* is a list of solvents ranked according to their eluting power.

A *chromatogram* is a plot of the detector's signal as function of elution time or volume.

The *distribution constant* for a solute in chromatography is equal to the ratio of its molar analytical concentration in the stationary phase to its molar analytical concentration in the mobile phase.

The *retention time* (t_r) is the time a solute takes to move from the point of injection to the detector. The *retention volume* (V_r) is the volume of mobile phase needed to move a solute from its point of injection to the detector. The *dead time* or *void time* (t_m) is the time required for unretained solutes to move from the point of injection to the detector. The *void volume* is the volume of mobile phase needed to move an unretained solute from the point of injection to the detector. The *adjusted retention time* (t_r') is the difference between a solute's retention time and column's void time.

The *baseline width* (w) is the width of a solute's chromatographic band measured at the baseline. *Band broadening* is the increase in a solute's baseline width as it moves from the point of injection to the detector. The *resolution* R_s of a column provides a quantitative measure of its ability to separate two analytes. The *capacity factor* (k') is a measure of how strongly a solute is retained by the stationary phase. The *selectivity factor* (α) is the ratio of capacity factors for two solutes showing the column's selectivity for one of the solutes. The *theoretical plate* is a quantitative means of evaluating column efficiency that treats the column as though it consists of a series of small zones, or plates, in which partitioning between the mobile and the stationary phases occurs. A column's *peak capacity* (n_c) is the maximum number of solutes that can be resolved on a particular column.

7.8.2 Classification of Chromatographic Methods

1. Techniques by Chromatographic Bed Shape

Column chromatography is a separation technique in which the stationary phase is placed in a narrow column through which the mobile phase moves under the influence of gravity or pressure. The stationary phase is either a solid or a thin, liquid film coating on a solid particulate packing material or the column's walls. Differences in rates of movement through the medium are calculated to different retention times of the sample.

Planar chromatography is a separation technique in which the stationary phase is immobilized on a flat surface. The plane can be a paper, serving as such or impregnated by a substance as the stationary bed (*paper chromatography*) or a layer of solid particles spread on a support such as a glass plate (*thin layer chromatography*). Different compounds in the sample mixture travel different distances according to how strongly they interact with the stationary phase as compared to the mobile phase. The specific *retention factor* (R_f) of each chemical can be used to aid in the identification of an unknown substance.

2. Techniques by Physical State of Mobile Phase

Gas chromatography (GC), also sometimes known as *Gas-Liquid chromatography* (GLC), is a separation technique in which the mobile phase is an inert gas (most often Helium). The stationary phase is adhered to the inside of a small-diameter glass tube (a *capillary column*) or a solid matrix inside a larger metal tube (a *packed column*). Gas chromatography (GC) is based on a partition equilibrium of analyte between a solid stationary phase and a mobile gas. Gas chromatography is useful for the analysis of volatile components.

Liquid chromatography (**LC**) is a separation technique in which the mobile phase is a liquid. Liquid chromatography can be carried out either in a column or a plane. Present day liquid chromatography that generally utilizes very small packing particles and a relatively high pressure is referred to as **high performance liquid chromatography** (**HPLC**). In the HPLC technique, the sample is forced through a column that is packed with irregularly or spherically shaped particles, a porous monolithic layer (stationary phase) or a porous membrane by a liquid (mobile phase) at high pressure. In HPLC, the mobile phase is either a nonpolar solvent (*normal phase*) or a polar solvent (*reverse phase*). HPLC can be applied to a wider range of samples than GC; however, the separation efficiency for HPLC is not as good as that for GC.

Together, GC and HPLC account for the largest number of chromatographic separations.

Affinity chromatography (AC) is a liquid chromatographic technique that uses a well-defined binding agent as a stationary phase for the selective purification or analysis of sample components. It is very specific, but not very robust. It is often used in biochemistry in the purification of proteins bound to tags. These fusion proteins are labeled with compounds such as His-tags, biotin or antigens, which bind to the stationary phase specifically. After purification, some of these tags are usually removed and the pure protein is obtained.

Supercritical fluid chromatography is a separation technique in which the mobile phase is a fluid above and relatively close to its critical temperature and pressure.

3. Techniques by Separation Mechanism

Ion exchange chromatography uses ion exchange mechanism to separate analytes. It is usually performed in columns but can also be useful in planar mode. Ion exchange chromatography uses a charged stationary phase to separate charged compounds including amino acids, peptides, and proteins. In conventional methods the stationary phase is an *ion exchange resin* that carries charged functional groups which interact with oppositely charged groups of the compound to be retained. Ion exchange chromatography is commonly used to purify proteins using *fast protein liquid chromatography* (FPLC).

Size-exclusion chromatography (SEC), also known as **gel permeation chromatography** (GPC), separates molecules according to their *size* (or more accurately according to their *hydrodynamic diameter* or *hydrodynamic volume*). It is based on the ability of molecules to move through a column of gel that has pores of clearly-defined sizes. The larger molecules can not enter the pores, thus they pass quickly through the column and elute first. Slightly smaller molecules can enter some pores, and so take longer to elute, and small molecules can be delayed further. The technique can be used to determine the molecular weight of large biomolecules and polymers, as well as separating them from salts and small molecules. It is also useful for determining the tertiary structure and the quaternary structure of purified proteins, especially since it can be carried out under native solution conditions.

7.8.3 Electrophoretic Methods

Electrophoresis is a separation method based on the differential rates of migration of charged species in an applied direct-current (DC) electric field. Electrophoresis on a macro scale has been applied to a variety of difficult analytical separation problems: inorganic anions and cations, amino acids, catecholamines, drugs, vitamins, carbohydrates, peptides, proteins, nucleic acids, nucleotides, polynucleotides, and numerous other species. A particular strength of electrophoresis is its unique ability to separate charged macromolecules of interest to biochemists, biologists, and clinical chemists.

In *capillary zone electrophoresis* a sample's components are separated based on their ability to move through a conductive medium under the influence of an applied electric field. Because of the effect of *electroosmotic flow*, positively charged solutes elute first, with smaller, more highly charged cationic solutes eluting before larger cations of lower charge. Neutral species elute without undergoing further separation. Finally, anions elute last, with smaller, more negatively charged anions being the last to elute. By adding a surfactant, neutral species also can be separated by *micellar electrokinetic capillary chromatography*. Electrophoretic separations also can take advantage of the ability of polymeric gels to separate solutes by size (*capillary gel electrophoresis*) and the ability of solutes to partition into a stationary phase (*capillary electrochromatography*). In comparison to GC and HPLC, capillary electrophoresis provides faster and more efficient separations.

7.9 Some Other Important Analytical Methods

Microscopy is the technical field of using microscopes to view samples or objects that cannot be seen with the unaided eye. There are three well-known branches of microscopy, *optical*, *electron*, and *scanning probe microscopy*. Optical and electron microscopy involve the *diffraction*, *reflection*, or *re-*

fraction of electromagnetic radiation/electron beams interacting with the subject of study, and the subsequent collection of this scattered radiation in order to build up an image. **Scanning electron microscopy** (SEM) and **transmission electron microscopy** (TEM) are the most widely used electron microscopies. *Scanning probe microscopy* (SPM) involves the interaction of a scanning probe with the surface or object of interest. Scanning probe techniques such as **scanning tunneling microscopy** (STM), **atomic force microscopy** (AFM), and others, achieve atomic resolution.

Thermogravimetry (TG) is possibly the most widely used technique in thermal analysis. It involves the measurement of the mass of a substance as a function of temperature while the substance is subjected to a controlled temperature program. **Differential thermal analysis** (DTA) is a technique in which the *temperature difference* between a substance and a reference material is measured as a function of temperature while the system is subjected to a controlled temperature program. **Differential scanning calorimetry** (DSC) is a technique in which the difference in *heat flow* to a sample and to a reference is monitored against temperature while the entire system is subjected to a controlled temperature program. **Dynamic mechanical analysis** (DMA) is the technique of applying a stress or strain to a sample and analyzing the response to obtain phase angle and deformation data.

Raman spectroscopy (RS) is based on an incoherent inelastic scattering process of light by matter, in either its solid, liquid, or gas state. This interaction between ultraviolet (UV), visible (VIS) or near-infrared (NIR) photons with matter gives rise to a Raman spectrum characterizing its different vibrational transitions. These vibrational transitions may be active for the infrared (IR) absorption or the Raman scattering processes, or for both of them, depending on their selection rules and so IR frequencies may be present or absent in the Raman spectrum of a compound and vice versa. IR and RS are therefore closely related.

Auger electron spectroscopy (AES) is an electron energy spectroscopy which probes the electronic energy levels of atoms, using electron or X-ray beam stimulation. Irradiation of a sample with one of these stimuli causes electron emissions which can be analyzed to obtain an energy distribution. Since the energies of the Auger electrons are characteristic of the atomic core valence level energies, they contain chemical information about their source atoms. As a result, the recorded energy spectra can be analyzed to determine the atomic composition (atomic percent) of the sample, and in some cases, extract chemical bonding information.

Photoelectron spectroscopy (**PES**) is widely used for the chemical analysis of solid surfaces. When ultraviolet (UV) light or X-rays are incident upon a solid surface, electrons are emitted via the photoelectric effect. PES involves measurements of the kinetic energy distribution of the emitted electrons. When PES is used to measure the core-level, or inner-shell, electrons using a conventional X-ray tube, it is known as XPS or *electron spectroscopy for chemical analysis* (*ESCA*). **X-ray photoelectron spectroscopy** (**XPS**) is widely used to measure the composition and chemical states of species in the near-surface region of a solid material in ultrahigh vacuum (UHV). The spectra provide information related to the electronic structure and the chemical composition of the near- surface region and to the bonding of adsorbates onto the surface.

X-ray methods covers many techniques based on the scatter, emission and absorption properties of X-radiation, the two most common are **X-ray fluorescence** (**XRF**) spectrometry and **X-ray powder diffractometry** (**XRD**). The scope of materials analysis that can be provided by X-ray diffraction includes crystalline phase identification, lattice parameter measurement, grain size measurement, and texture analysis.

Electrochemiluminescence (ECL) is a term commonly applied to systems in which transfer reactions of electrogenerated species occur to produce excited states, usually with regeneration of luminescent species.

References

[1] Skoog D A, West D M, Holler F J, Crouch S R. Analytical chemistry: an introduction: seventh edition [M]. Belmont: Thomson Brooks/Cole, 1999.

[2] Harvey D. Modern analytical chemistry [M]. Boston: McGraw - Hill Companies, Inc., 2000.

[3] Robert A M (editor - in chief). Encyclopedia of analytical chemistry: applications, theory and instrumentation [M]. New York: John Wiley & Sons Inc., 2000.

[4] Budnikov G K, Electrochemical methods of analysis [J]. Journal of Analytical Chemis-

try, 2000(55): 1007.

[5] http://en.wikipedia.org/wiki/Analytical_chemistry.

[6] http://www.chem.utoronto.ca/research/analytical.php.

[7] http://www.reagents.com/products/reagents/grades.html.

[8] http://encyclopedia 2.thefreedictionary.com/Reagent, + Chemical.

[9] http://www.csudh.edu/oliver/che230/textbook/ch05.htm.

[10] http://www.britannica.com/EBchecked/topic/242396/gravimetric - analysis.

[11] http://en.wikipedia.org/wiki/Gravimetric_analysis.

[12] http://www.chemtech.org/cn/cn206/206 - 4.htm.

[13] http://www.britannica.com/EBchecked/topic/486122/quantitative - chemical - analysis.

[14] http://en.wikipedia.org/wiki/Titration.

[15] http://en.wikipedia.org/wiki/Electroanalytical_method.

[16] http://encyclopedia2.thefreedictionary.com/Electrochemical + Methods + of + Analysis.

[17] http://www.oup.co.uk/pdf/0 - 19 - 850477 - 2.pdf.

[18] http://electrochem.cwru.edu/encycl/art - a03 - analytical.htm.

[19] http://electrochem.cwru.edu/ed/dict.htm.

[20] http://www.cem.msu.edu/~reusch/VirtTxtJml/Spectrpy/spectro.htm.

[21] http://chemistry.about.com/od/analyticalchemistry/a/spectroscopy.htm.

[22] http://www.wikidoc.org/index.php/UV/VIS_spectroscopy.

[23] http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/uvvisab1.htm.

[24] http://teaching.shu.ac.uk/hwb/chemistry/tutorials/.

[25] http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/MassSpec/masspec1.htm.

[26] http://en.wikipedia.org/wiki/Mass_spectrometry.

[27] http://www.files.chem.vt.edu/chem - ed/crossref/ac - mass - spec.html.

[28] http://en.wikipedia.org/wiki/Nuclear_magnetic_resonance.

[29] http://www.cis.rit.edu/htbooks/nmr/inside.htm.

[30] http://www.andor.com/learning/applications/Atomic_Spectroscopy/.

[31] http://en.wikipedia.org/wiki/Atomic_absorption_spectroscopy.

[32] http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/chrom1.htm.

[33] http://en.wikipedia.org/wiki/Chromatography.

[34] http://en.wikipedia.org/wiki/Microscopy.

Chapter 8 Polymer Chemistry

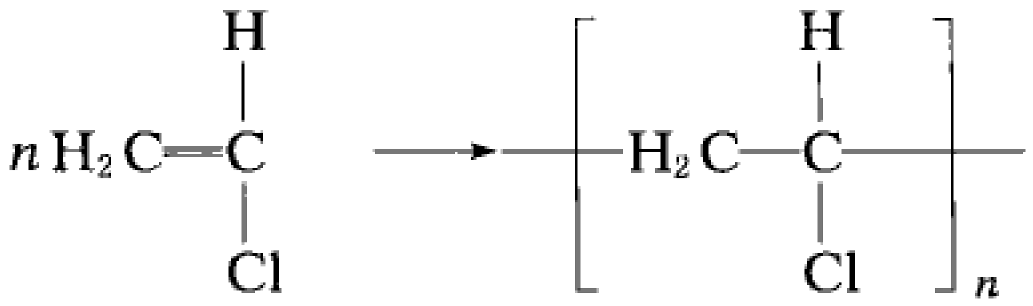
Polymers are formed by the linking of numerous separate small **monomer** units in strands and webs and are ubiquitous both in nature and in modern industrial chemistry. Most foods and fibers are polymers. The diverse, useful materials lumped under the name "plastic" are synthetic (or semi-synthetic) carbon-based polymers. Natural carbon-based polymers include energy-storage and structural materials (such as starch, cellulose, and protein), the enzymes that catalyze essential biochemical reactions, and the genetic substances DNA and RNA, which store and transmit the information required for the replication of life. The prominence of carbon-based polymers in biology and industry sometimes obscures the many polymers that contain no carbon whatever. The chains of alternating Si and O atoms found in some silicate minerals and in synthetic silicones are examples.

8.1 Synthetic Polymers

To construct a polymer a very large number of monomer units must add to a growing polymer molecule; the reaction must not falter after the first few molecules have reacted. Continued growth is achieved by having the polymer molecule retain highly reactive functional groups at all times during its synthesis. The two major types of polymerization reaction are addition polymerization and condensation polymerization.

8.1.1 Addition Polymerization

In **addition polymerization**, monomers react to form a polymer chain without net loss of atoms. The most common type of addition polymerization involves **free-radical chain reaction** of molecules that have C = C double bonds. As an example, consider the polymerization of vinyl chloride (chloroethylene, $CH_2{=}CHCl$) to polyvinyl chloride:



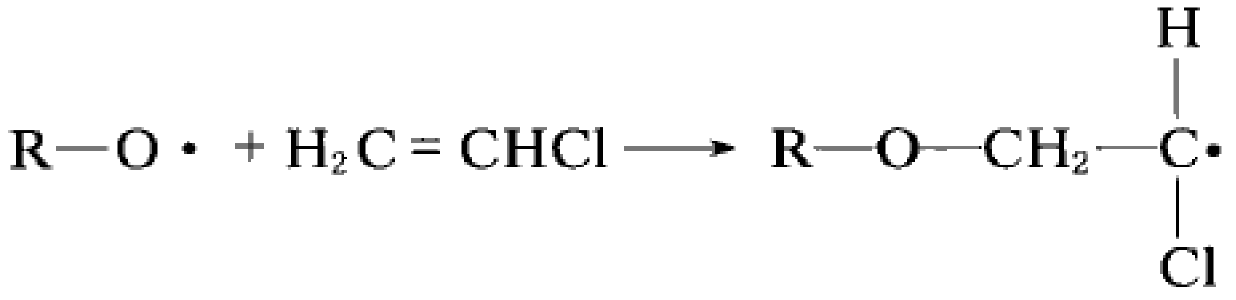
$$n\,\mathrm{H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}} \longrightarrow \left[\mathrm{H_2C{-}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}}\right]_n$$

The overall process consists of three steps: **initiation**, **propagation** (repeated many times to build up a long chain), and **termination.**

The polymerization of vinyl chloride can be initiated by a small concentration of molecules that have bonds weak enough to be broken by the action of light or heat, giving radicals. An example of such an **initiator** is a *peroxide*, which can be represented as $\mathrm{R{-}O{-}O{-}R'}$, where R and R′ represent alkyl groups. The weak O—O bonds can break to give radicals:

$$\mathrm{R{-}O{-}O{-}R'} \longrightarrow \mathrm{R{-}O\cdot} + \mathrm{\cdot O{-}R'} \quad \text{(initiation)}$$

The radicals react avidly with vinyl chloride, accepting electrons from the C = C double bonds to re-establish a closed-shell electron configuration on the oxygen atoms:



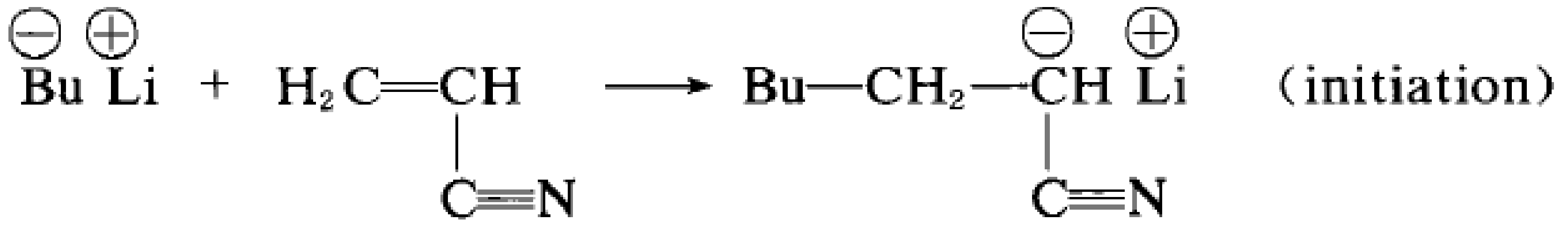
$$\mathrm{R{-}O\cdot} + \mathrm{H_2C{=}CHCl} \longrightarrow \mathrm{R{-}O{-}CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}\cdot} \quad \text{(propagation)}$$

One of the two π-electrons in the vinyl chloride double bond has been used to form a single bond with the $\mathrm{R{-}O\cdot}$ radical. The other remains on the second carbon atom, leaving it as a seven-valence-electron atom that reacts with another vinyl chloride molecule. At each stage, the *end - group* of the lengthening chain is left one electron and remains quite reactive. The reaction can continue, building up long-chain molecules of high molecular mass. The vinyl chloride monomers always attach to the growing chain with their $\mathrm{CH_2}$ group, because the odd electron is more stable on a CHCl end-group. This gives the polymer a regular alternation of $\mathrm{{-}CH_2{-}}$ and $\mathrm{{-}CHCl{-}}$ groups.

Termination occurs when the radical end-groups on two different chains encounter each other and the two chains couple to give a longer chain. Alternatively, a hydrogen atom may transfer from one end-group to the other. The latter termination step leaves a double bond on one chain end and a $\mathrm{{-}CH_2Cl}$ group on the other. When polymer molecules are long, the exact nature of the end-groups has little effect on the physical and the chemical properties of the material.

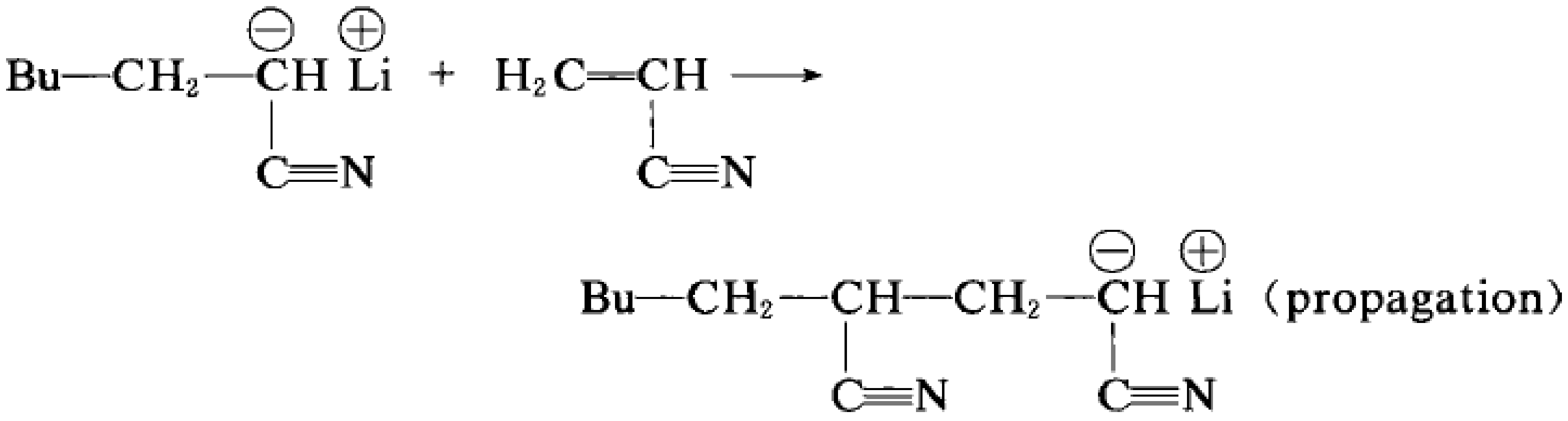
A different type of *hydrogen-transfer step* often has a much larger effect on the properties of the resulting polymer. Suppose that hydrogen-atom transfer occurs not from the monomer unit on the end of a second chain, but from a monomer unit in the middle of that chain. Then the first chain stops growing, but the radical site moves to the middle of the second chain, and growth resumes from that point, forming a branched polymeric chain with very different properties.

Addition polymerization can be initiated by ions as well as by free radicals. An example is the polymerization of *acrylonitrile*. A suitable initiator for this process is *butyl lithium* [$(CH_3CH_2CH_2CH_2)^- Li^+$]. The butyl anion (abbreviated Bu^-) reacts with the end carbon atom in a molecule of acrylonitrile to give a new anion:



$$\overset{\ominus}{\mathrm{Bu}}\ \overset{\oplus}{\mathrm{Li}} + \mathrm{H_2C{=}}\underset{\mathrm{C{\equiv}N}}{\mathrm{CH}} \longrightarrow \mathrm{Bu{-}CH_2{-}}\underset{\mathrm{C{\equiv}N}}{\overset{\ominus}{\mathrm{CH}}}\ \overset{\oplus}{\mathrm{Li}} \quad \text{(initiation)}$$

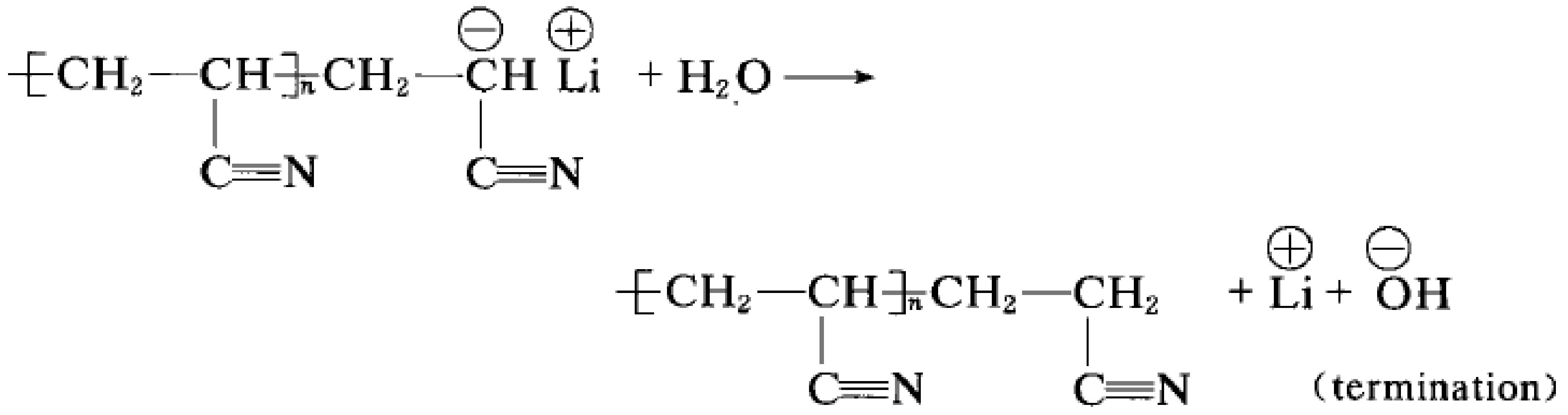
The new anion then reacts with an additional molecule of acrylonitrile according to



$$\mathrm{Bu{-}CH_2{-}}\underset{\mathrm{C{\equiv}N}}{\overset{\ominus}{\mathrm{CH}}}\ \overset{\oplus}{\mathrm{Li}} + \mathrm{H_2C{=}}\underset{\mathrm{C{\equiv}N}}{\mathrm{CH}} \longrightarrow \mathrm{Bu{-}CH_2{-}}\underset{\mathrm{C{\equiv}N}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\mathrm{C{\equiv}N}}{\overset{\ominus}{\mathrm{CH}}}\ \overset{\oplus}{\mathrm{Li}} \quad \text{(propagation)}$$

The process continues, building up a long-chain polymer.

Ionic polymerization differs from free-radical polymerization because the negatively charged end-groups repel one another, ruling out the coupling of two active chains. The ionic group at the end of the growing polymer is stable at each stage. Once the supply of monomer has been used up, the polymer can exist indefinitely with its ionic end-group, in contrast with the free-radical case, in which some reaction must take place to terminate the process. Ion-initiated polymers are called "**living polymers**" because when additional monomer is added (even months later), they resume growth and increase in molecular mass. Termination can be achieved by adding water to replace the Li^+ with a hydrogen ion:

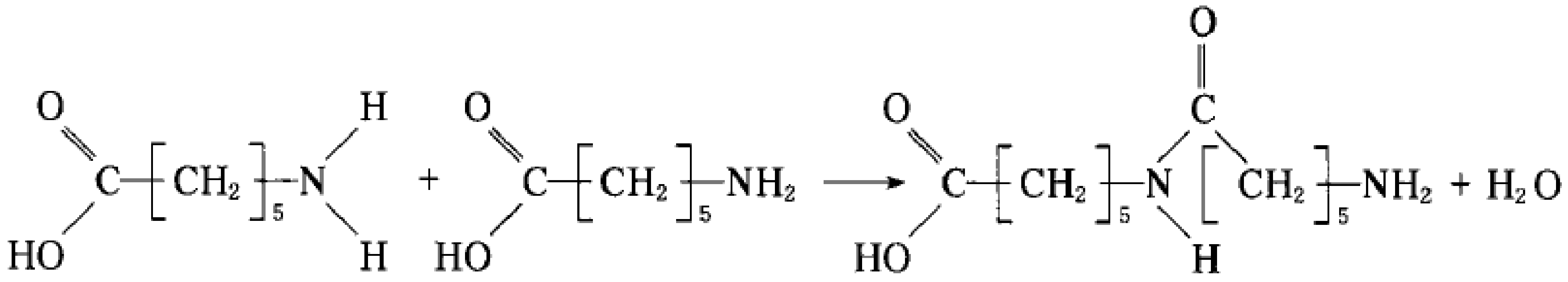


$$\left[CH_2-\underset{C\equiv N}{CH}\right]_n CH_2-\underset{C\equiv N}{\overset{\ominus}{C}H}\ \overset{\oplus}{Li} + H_2O \longrightarrow \left[CH_2-\underset{C\equiv N}{CH}\right]_n CH_2-\underset{C\equiv N}{CH_2} + \overset{\oplus}{Li} + \overset{\ominus}{OH}$$

(termination)

8.1.2 Condensation Polymerization

A second important mechanism for polymerization is **condensation polymerization**, in which a small molecule (frequently water) is split off as each monomer unit is attached to the growing polymer. An example is the polymerization of *6-aminohexanoic acid*. The first two molecules react upon heating according to



An *amide linkage* and water form from the reaction of an amine with a carboxylic acid. The new molecule still has an amine group on one end and a carboxylic acid group on the other end, so it can react with two more molecules of 6-aminohexanoic acid. The process repeats to build up a long-chain molecule. For each monomer unit added, one molecule of water is split off. The final polymer in this case is called "*nylon-6*".

Addition and condensation polymerization differ in the distribution of chain lengths over the course of the reaction. In addition polymerization, reaction begins only at the initiator sites, so relatively few polymer chains are growing at any one time. If the reaction is interrupted short of completion, the result is a number of polymer molecules mixed with unreacted monomer. In condensation polymerization, every monomer is a potential initiator, and so *dimers* and *trimers* begin to form throughout the mixture almost immediately upon heating. If the reaction is stopped short of completion, the mixture contains a large number of "**oligomers**" (molecules with short polymer chains) and almost no monomer. If the reaction later resumes, the oligomers react with each other to give long-chain polymers.

Copolymers

A **copolymer** is a polymer formed from two or more different monomers. Consider *butadiene* and *styrene* (vinyl benzene). Free-radical initiation causes each of these compounds to polymerize. The polymerization of styrene to polystyrene proceeds similarly to the polymerization of vinyl chloride outlined at the beginning of this section. Butadiene has two C=C bonds per monomer, and its polymerization is different and interesting. The π-electrons shift upon initiation and during propagation, causing the systematic relocation of double bonds:

$$R{-}O\cdot + H_2C{=}CH{-}CH{=}CH_2 \longrightarrow R{-}O{-}CH_2{-}CH{=}CH{-}CH_2\cdot$$

(initiation)

One π-electron from each of the two double bonds has moved to the central C—C bond, converting it into a double bond. A third π-electron is used to make the O—C bond to the initiator, and the fourth remains as an unpaired electron on the terminal —CH_2 group, ready to react further according to

$$R{-}O{-}CH_2{-}CH{=}CH{-}CH_2\cdot + H_2C{=}CH{-}CH{=}CH_2 \longrightarrow$$
$$R{-}O{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2\cdot \text{ (propagtion)}$$

In the *polybutadiene* that ultimately forms, $-(CH_2{-}CH{=}CH{-}CH_2)_n-$, all the C—C single bonds from the monomers have been converted into double bonds, and all the double bonds have become single bonds.

Now let us suppose that polymerization is initiated in a mixture of styrene and butadiene. In this case, the growing polymer chain may encounter and react with either type of monomer. The result is a **random copolymer**, with butadiene (B) and styrene (S) units in an *irregular* sequence along the chain. The probability of attachment of a given type of monomer unit depends not only on its *concentration* in the mixture but also on its inherent *reactivity*. Thus, the fraction of B monomer units in a chain does not generally equal the fraction of B in the original mixture. Nonetheless, varying the composition of the mixture does change the ratio of the two monomer units in the polymer that results. For example, a 1 : 6 molar ratio of styrene to butadiene monomers is used to make styrene-butadiene rubber (SBR) for automobile tires, and a 2 : 1 ratio gives a copolymer used in latex paints.

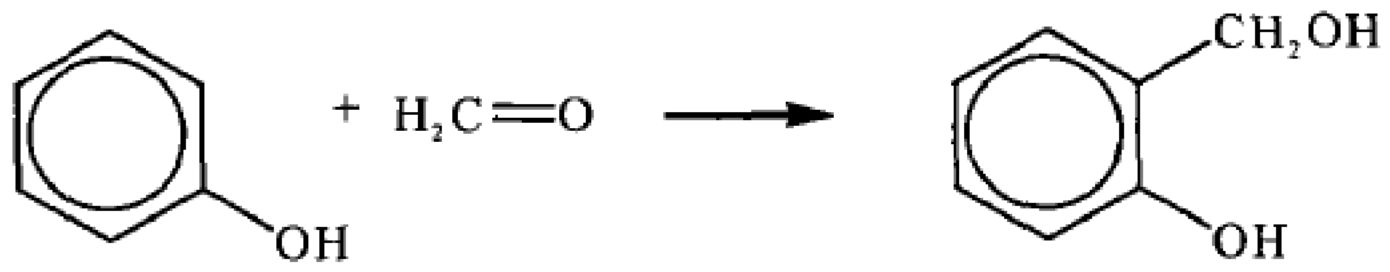
A second type of copolymer is called a **block copolymer**. It consists of a series of blocks connected together, in which each block is a chain of one type of monomer unit. In a typical block copolymer of butadiene and styrene, a large block of butadiene units and a large block of styrene units are linked to form the final polymer chain. More complicated block copolymers might have several alternating blocks. Such copolymers can be made by using the "living-polymer" process described earlier: polymerization in pure butadiene is initiated by butyl lithium and allowed to proceed until long chains are created and the butadiene is used up, after which some styrene is added and the chains grow further with styrene units. Block copolymers have very different properties from random ones. They also differ from simple mixtures of two polymers. A mixture of polystyrene and polybutadiene tends to separate into two phases, each rich in one of the polymers. This cannot occur in a copolymer because the polystyrene and the polybutadiene portions of the chain are connected by a chemical bond.

A third type of copolymer is called a **graft copolymer**. It is made by polymerizing one component and then "grafting on" side-chains of the second to the chains of the first. In *high-impact polystyrenes*, for example, a small amount of butadiene is polymerized first. Upon addition of styrene and a free-radical initiator, radical sites are formed along the polybutadiene chain and serve as starting points for polystyrene growth. The result is a polybutadiene chain onto which are grafted a series of polystyrene chains, just as branches can be grafted onto tree limbs in an orchard. The resulting plastic is significantly harder and more resistant to impact than ordinary polystyrene.

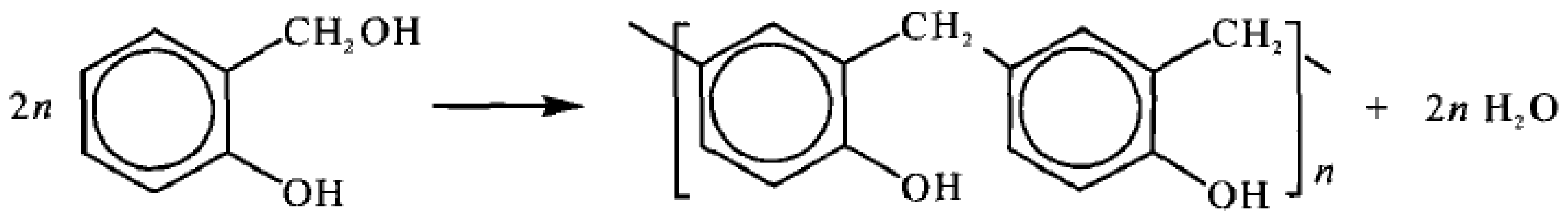
Cross-Linking

If every monomer forming a polymer has only two reactive sites, then only *chains* and *rings* can be made. However, if some or all of the monomers in a polymer have three or more reactive sites, then **cross-linking** is possible to form *sheets* or *networks*. This is often desirable in synthetic polymers because it leads to a stronger material.

One important example of cross-linking involves copolymers of *phenol* and *formaldehyde*. When these two compounds are mixed with the phenol in excess (in the presence of an acid catalyst), straight-chain polymers form. The first step is the addition of formaldehyde to phenol to give *methylolphenol*:



Molecules of *hydroxymethylphenol* can then react through condensation polymerization (releasing water) to form a linear polymer called *novalac*:



If, on the other hand, the reaction is carried out with an excess of formaldehyde, then *di-* and *trihydroxymethylphenols* form. Each of these monomers has more than two reactive sites and can react with up to three others to form the type of cross-linked structure. The cross-linked polymer is much stronger than the linear polymer. The very first synthetic plastic, *Bakelite*, was made in 1907 from cross-linked phenol and formaldehyde. Modern phenol-formaldehyde polymers are used extensively in the construction industry as adhesives for plywood.

Cross-linking is often desirable because it leads to a stronger material. Sometimes cross-linking agents are added deliberately to form additional bonds between polymer chains. Polybutadiene, for example, contains double bonds that can be linked upon addition of appropriate oxidizing agents. One especially important kind of cross-linking occurs through sulfur chains in rubber.

8.1.3 Characterization of polymers

1. Molecular Weight

All synthetic polymers consist of molecules with different weights and are said to be **polydisperse**. The average molecular weight of a polymer is the product of the average number of repeating units times the molecular weight of these repeating units. The **number-average molecular weight** M_n is calculated by dividing the sum of the individual molecular weight values by the number of molecules. Most thermodynamic properties are related to the number of particles present and thus dependent on M_n. The **weight-average molecular weight** M_w is defined as:

$$M_w = \frac{\sum N_i M_i{}^2}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum W_i}$$

where N_i is the number of molecules of molecular weight M_i, and W_i is the weight of molecules of molecular weight M_i. M_w is always greater than M_n except in **monodisperse** system because the calculation for M_w give more emphasis to the larger molecule, while M_n calculation give equal emphasis to all molecules. The ratio $\frac{M_w}{M_n}$ is a measure of molecular weight distribution and is called the **polydispersity index**. The most popular technique for measuring distributions of molecular weights is known as **gel permeation chromatography** (GPC).

2. Glass Transition Temperature

All linear polymers are glasses at low temperatures. As the temperature is raised, a certain point is reached at which the polymer changes from a glass to a rubber. This change is known as the **glass transition temperature** (T_g). This transition is characteristic of a particular polymer in much the same way that a melting point is characteristic of ordinary low-molecular-weight compounds. To a very large extent, the practical utility of polymers and their different properties depend heavily on their glass transition temperatures. **Differential thermal analysis** (DTA) and **differential scanning calorimetry** (DSC) are perhaps the most popular techniques for the measurement of glass transition temperatures.

3. Polymer Structure Determination

Many methods are available for the determination of molecular structures of polymers. These include *infrared* and *ultraviolet spectroscopy*, *opti-*

cal rotatory dispersion (ORD), *nuclear magnetic resonance* (NMR), *light scattering*, *ultracentrifugation*, *GPC*, *conformational analysis*, and *X-ray crystallography*. In practice, NMR and X-ray crystallography have proved to be especially useful. The *X-ray diffraction* (XRD) method is the most powerful technique available for the examination of ordered polymers in the solid state. Generally, if the polymer forms oriented fibers, is microcrystalline, or yields single crystals useful information about the molecular structure can be obtained including the chain conformation and the position of individual atoms.

8.2 Natural Polymers

All the products of human ingenuity in the design of polymers pale beside the products of nature. Plants and animals employ a tremendous variety of long-chain molecules with different functions: some for structural strength, others to act as catalysts, and still others to provide instructions for the synthesis of vital components of the cell. In this section, we discuss two important classes of natural polymers: proteins and carbohydrates.

8.2.1 Amino Acids

The monomeric building blocks of the important biopolymers called proteins are the **α-amino acids**. The simplest amino acid is *glycine*. An amino acid contains an amine group ($—NH_2$) and a carboxylic-acid group ($—COOH$). In α-amino acids, the two groups are bonded to the same carbon atom. In acidic aqueous solution, the amine group of an amino acid gains a hydrogen ion to form $—NH_3^+$; in basic solution, the carboxylic acid group loses a hydrogen ion to form $—COO^-$. At intermediate pH, both reactions occur, that is, the hydrogen ion transfers from the carboxylic acid group to the amine group.

Two glycine molecules can condense with loss of water to form an amide. The amide functional group connecting two amino acids is referred to as a **peptide linkage**, and the resulting molecule is called a dipeptide—in this case, *diglycine*. Because the two ends of the molecule still have carboxylic acid and amine groups, further condensation reactions to form a **polypeptide**, a polymer composed of many amino-acid groups, are possible. If glycine were the only amino acid available, the result would be *polyglycine*, a rather uninteresting protein. Of course, nature does not stop with glycine as a monomer unit. Any of 20 different α-amino acids are found in most natural polypeptides. In each of these, one of the two hydrogen atoms on the central carbon atom of glycine is replaced by another side-group.

8.2.2 Proteins

A **protein** is a long polypeptide made by joining α-amino acids through peptide linkages. The term is usually applied to polymers having more than about 50 amino-acid groups; large proteins may contain many thousand such monomer units. Given the fact that any one of 20 α-amino acids may appear at each point in the chain, the number of possible sequences of amino acids in even small proteins is staggering. Moreover, the *amino-acid sequence* describes only the first aspect of the molecular structure of a protein. It contains no information about the three-dimensional conformation adopted by the protein. The $C=O$ group and the $N—H$ group in each amino acid along the protein chain are potential sites for hydrogen bonds. Hydrogen bonds may also involve functional groups on the amino-acid side-chains. Also, the *cysteine* side-groups ($—CH_2—SH$) can react with one another, with loss of hydrogen, to form $—CH_2—S—S—CH_2—$ disulfide bridges between different cysteine groups in a single chain or between neighboring chains (the same kind of cross-linking by sulfur occurs in the *vulcanization* of rubber). As a result of these strong intrachain interactions, the molecules of a given protein have a rather well-defined conformation even in solution, as compared with the much more varied range of conformations available to a simple alkane chain. The three-dimensional structures of many proteins have been determined by X-ray diffraction. This method relies on getting the protein to crystallize, something that is often hard to do. Nonetheless, these determinations are the main source of information about protein structure.

There are two primary categories of proteins: fibrous and globular. **Fibrous proteins** are usually structural materials in nature. They consist of sheets of regularly linked polymer chains or else of long fibers comprising protein chains twisted into spirals. Silk is a fibrous protein in which the monomer units are primarily glycine and alanine, with smaller amounts of serine and tyrosine.

The second type of protein is the **globular protein**. Globular proteins include the carriers of oxygen in the blood (*hemoglobin*) and in cells (*myoglobin*). They have irregular folded structures and typically consist of between 100 and 1000 amino-acid groups in one or more chains.

Enzymes constitute a very important class of globular protein. They catalyze nearly every reaction in living cells, such as those synthesizing or breaking down other proteins, transporting substances across cell walls, or recognizing and resisting foreign bodies. Enzymes must have two characteristics: they must be effective in lowering the activation barrier for a reaction, and they must be selective so as to act only on a restricted group of substrates.

8.2.3 Carbohydrates

Glucose ($C_6H_{12}O_6$) is a leading representative of a class of organic compounds called **carbohydrates**. Carbohydrates are widely distributed natural products, most of which are produced photosynthetically from carbon dioxide and water by growing plants. Their name comes from the form of their chemical formulas, which can be written as $C_n(H_2O)_m$, suggesting a "hydrate" of carbon. Simple **sugars**, or **monosaccharides**, are carbohydrates with the chemical formula $C_nH_{2n}O_n$. Those with three, four, five, and six carbon atoms are called *trioses*, *tetroses*, *pentoses*, and *hexoses*, respectively.

Many plant cells do not stop the process of *photosynthesis* with simple sugars like glucose but continue by linking sugars together as monomer units to form more complex carbohydrates. **Disaccharides** are composed of two simple sugars linked together in a condensation reaction, with the elimination of water. The different sugars differ in their sweetness. *Fructose* is sweeter than *sucrose*, which is sweeter than *glucose*. It follows that fructose is a lower-calorie natural sugar because less of it gives the same sweet taste. Sucrose solutions can be treated with an enzyme called *invertase*, which hydrolyzes the bond between the two rings and leaves a mixture of fructose and glucose, called invert sugar, which is sweeter than the original sucrose because of its fructose content.

Further linkages of sugar units lead to polymers called **polysaccharides**. The position of the oxygen atom linking the monomer units has a profound effect on the properties and the function of the polymers that result. *Starch* is a polymer of *α-D-glucose* and is metabolized by humans and animals. *Cellulose*, a polymer of *β-D-glucose* can be digested only by certain bacteria that live in the digestive tracts of goats, cows, and other ruminants, and in some insects, such as termites. It forms the structural fiber of trees and plants and is present in linen, cotton, and paper. It is the most abundant organic compound on earth. Despite the great solubility of the monomer D-glucose in water, neither starch nor cellulose is water soluble.

8.3 Applications of Polymers

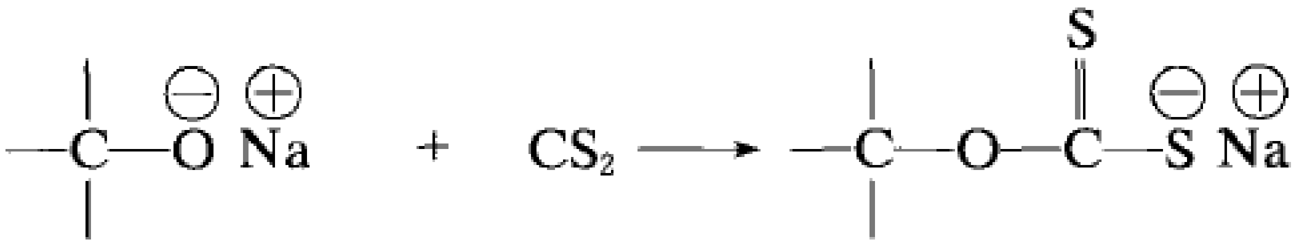
If food is excluded, the three largest uses for polymers are in *fibers*, *plastics*, and *elastomers* (*rubbers*). These three types of materials are distinguished on the basis of their physical properties, especially their resistance to *stretching*. A typical fiber strongly resists stretching and elongates by less than 10% before breaking. Plastics are intermediate in their resistance to stretching and elongate 20% to 100% before breaking. Elastomers stretch readily, with elongations of 100% to 1000% (that is, some rubbers can be stretched by a factor of 10 without breaking). In this section, we examine the major kinds of polymers and their uses.

8.3.1 Fibers

Many important fibers, including *cotton* and *wool*, are naturally occurring polymers. The origins of the modern synthetic fiber industry are said to lie in an accident in the laboratory of the German chemist Christian Schonbein, who in 1845 wiped up a spill of nitric and sulfuric acids with a cotton apron, hung up the apron to dry, and thereby produced the polymer *cellulose trinitrate* (guncotton). In guncotton, all three —OH groups in the glucose subunits of the cellulose are replaced by $—ONO_2$ nitrate groups. The compound is an explosive; it was subsequently developed into *cordite* and continues in extensive use today as a *propellant* in guns and rockets.

By varying the amounts of acid used, one can prepare a second nitrated derivative of cellulose. In *nitrocellulose* (*cellulose dinitrate*), only the two —OH groups directly attached to each ring are nitrated. When this compound is dissolved in a mixture of camphor and alcohol and the solvent carefully evaporated, the product is *celluloid*, a material used for photographic film in the early motion picture industry. The nitrate groups in celluloid make it quite flammable, as might be expected from a polymer closely related to guncotton. This fact, combined with the high price of camphor, led to the use of *cellulose acetate* instead of celluloid in photographic film. In cellulose acetate all three —OH groups on the glucose rings are esterified by treatment with acetic acid that contains a small amount of sulfuric acid to form $-OCOCH_3$ side-groups.

The discovery of nitrocellulose also led to the production of the first synthetic fiber. In 1884, the French chemist Hilaire Bernigaud showed how to remove the nitrate groups in nitrocellulose and to spin the resulting reconstituted cellulose into fibers. Modest commercial success for the resulting synthetic fiber ensued until the development of the alternative and cheaper **viscose rayon** some ten years later. In the viscose-rayon process, which is still used today, cellulose is digested in a concentrated solution of NaOH to convert the —OH groups into $-O^- Na^+$ ionic groups. Reaction with CS_2 leads to the formation of about one "*xanthate*" group for every two glucose monomer units:



$$-\underset{|}{\overset{|}{C}}-\overset{\ominus}{O}\ \overset{\oplus}{Na} + CS_2 \longrightarrow -\underset{|}{\overset{|}{C}}-O-\overset{S}{\overset{\|}{C}}-\overset{\ominus}{S}\ \overset{\oplus}{Na}$$

Xanthate

Such substitutions weaken the hydrogen-bond forces holding polymer chains together. In the ripening step, some of these xanthate groups are removed with regeneration of CS_2 and others migrate to the $-CH_2OH$ groups from the ring —OH groups. After this has taken place, sulfuric acid is added to neutralize the NaOH and to remove the remaining xanthate groups. At the same time, the viscose rayon is spun out to form fibers. The chemical composition of the completed rayon is very close to that of the cellulose that began the process, but the polymer molecules are stretched out and aligned in fibers.

Rayon is a semi-synthetic fiber because it is prepared from a natural polymeric starting material. The first truly synthetic polymeric fiber was nylon, which was developed in the 1930s by Wallace Carothers at the Du Pont Company. He knew of the condensation of an amine with a carboxylic acid to form an amide linkage and noted that if each molecule had two amine or carboxylic acid functional groups, then long-chain polymers could be formed. The specific starting materials upon which Carothers settled after a number of attempts were *adipic acid* and *hexamethylenediamine*. The two condense with loss of water. The resulting molecule has a carboxylic-acid group on one end (which can react with another molecule of hexamethylenediamine) and an amine group on the other end (which can react with another molecule of adipic acid). The process can continue indefinitely, leading to a polymer called *nylon*-66. The nylon is extruded as a thread or spun as a fiber from the melt. The combination of well-aligned polymer molecules and N—H···O hydrogen bonds between chains makes nylon one of the strongest materials known.

The designation "66" indicates that this nylon has six carbon atoms on the starting carboxylic acid and six on the diamine. Other nylons can be made with different numbers of carbon atoms. After nylon-66, the most important is called *nylon-6* and can be made from the polymerization of *6-aminohexanoic acid*. Note that this uses a monomer in which a single molecule has both a carboxylic acid and an amine group. Such a molecule can "bite its own tail" to form a cyclic molecule with loss of water. This compound, called *caprolactam*, is the normal starting material for the production of nylon-6, which is a little cheaper but not quite as strong as nylon-66. The bonding in these nylons is just like the bonding in naturally occurring polypeptides and proteins. Polyglycine could in fact be referred to as *nylon-2*, a simple polyamide in which each repeating unit contains two carbon atoms.

Just as a carboxylic acid reacts with an amine to give an amide, so it reacts with an alcohol to give an ester. This suggests the possible reaction of a dicarboxylic acid and a glycol (dialcohol) to form a polymer. The polymer produced most extensively in this way is *polyethylene terephthalate* (PET), which is built up from *terephthalic acid* (a benzene ring with —COOH groups on either end) and *ethylene glycol*. The polymer is referred to as "**polyester**". The planar benzene rings in this polymer make it stiffer than nylon, which has no aromatic groups in its backbone, and help to make polyester fabrics crush-resistant. The same polymer, when formed in a thin sheet rather than a fiber, is known as *Mylar*, a very strong film used for audio and video tapes.

A final class of polymer fibers are the **acrylics**, which are built up from the free-radical polymerization of acrylonitrile. The resulting polymer is then dissolved and spun into fibers as the solvent evaporates. Pure *polyacrylonitrile* has an inconveniently high melting point and cannot be dyed, so most acrylics are copolymers with vinyl acetate, vinyl chloride, styrene, or other monomers. The presence of chlorine atoms in the copolymer reduces the flammability of the fabric.

8.3.2 Plastics

Plastics are loosely defined as polymeric materials that can be molded or extruded into desired shapes and that harden upon cooling or solvent evaporation. Polymers that can be formed repeatedly by application of heat and pressure are called **thermoplastics**; those that can be formed only once are called **thermosets**. Rather than being spun into threads in which the molecules are aligned, as in fibers, plastics are cast into three-dimensional forms or spread into films for packaging applications. Although celluloid articles were fabricated by plastic processing by the late 1800s, the first important synthetic plastic was Bakelite, the phenol-formaldehyde resin whose cross-linking was discussed.

Ethylene ($CH_2=CH_2$) forms polyethylene through a free-radical-initiated addition polymerization mechanism at high pressures (1000 to 3000 atm) and temperatures (300 to 500℃), conditions that require elaborate equipment. The product is not the perfect linear chain implied by the simple equation. Free radicals frequently abstract hydrogen from the middles of chains in this synthesis. This means that the polyethylene is heavily branched with hydrocarbon side chains of varying lengths. It is called **low-density polyethylene** (LDPE) because the difficulty of packing the irregular side-chains gives it a lower density ($<0.94\ \mathrm{g \cdot cm^{-3}}$) than that of perfectly linear polyethylene. This irregularity also makes it relatively soft, so its primary uses are in coatings, plastic packaging, trash bags, and squeeze bottles in which softness is an advantage, not a drawback.

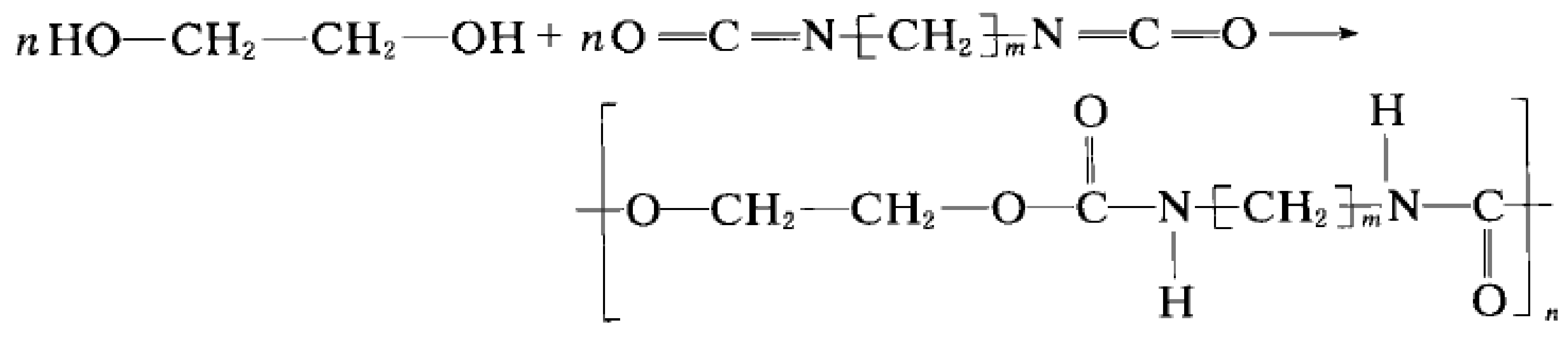
A major breakthrough occurred in 1954, when the German chemist **Karl Ziegler** showed that ethylene could also be polymerized with a catalyst consisting of $TiCl_4$ and an *organoaluminum* compound [for example, $Al(C_2H_5)_3$]. The addition of ethylene takes place at each stage within the coordination sphere of the titanium atom, so that monomer units can add only at the end of the growing chain. The result is linear polyethylene, also called **high-density polyethylene** (HDPE) because of its density ($0.96\ \mathrm{g \cdot cm^{-3}}$). Because its linear chains are so regular, HDPE contains large crystalline regions at low temperatures, which makes it much harder than LDPE and thus suitable for molding into plastic bowls, lids, and toys.

A third kind of polyethylene introduced in the late 1970s is called **linear low-density polyethylene** (LLDPE). This is made by the same metal-catalyzed reactions as HDPE, but it is a deliberate copolymer with other 1 - alkenes such as 1-butene. It has some side-groups, which reduce the crystallinity and the density, but these are of a controlled short length, as opposed to the irregular, long side-branches in LDPE. LLDPE is stronger and more rigid than LDPE; it is also cheaper because lower pressures and temperatures are used in its manufacture.

If one of the hydrogen atoms of the ethylene monomer unit is replaced with a different type of atom or functional group, the plastics that form upon polymerization have different properties. Substitution of a methyl group (that is, the use of propylene as monomer) leads to **polypropylene(pp)**. This reaction cannot be carried out successfully by free-radical polymerization, however. It was first performed in 1953 - 1954 by Ziegler and the Italian chemist **Giulio Natta**, who used the *Ziegler catalyst* employed in making HDPE. In polypropylene, the methyl groups attached to the carbon backbone can be arranged in different conformations. In the **isotactic** form, all the methyl groups are arranged on the same side, whereas in the **syndiotactic** form they alternate in a regular fashion. The **atactic** form shows a random positioning of methyl groups. Natta showed that the Ziegler catalyst led to isotactic polypropylene, and he developed another catalyst using VCl_4 that gave the syndiotactic form. Polypropylene plastic is stiffer and harder than HDPE and has a higher melting point, so it is particularly useful in applications in which somewhat higher temperatures are used (such as in the sterilization of medical instruments).

Substituting a chlorine atom for one of the hydrogen atoms in ethylene gives *vinyl chloride*, which polymerizes to **polyvinyl chloride** (PVC). The largest uses of PVC are in the construction industry, where a rigid and chemically resistant plastic is needed for making pipes and architectural products such as gutters, downspouts and siding. **Plasticizers** are frequently added to PVC to make it less rigid for other uses. A plasticizer is an additive that softens a plastic and makes it more flexible. In a rigid amorphous plastic, nonbonded attractions between the tangled molecules of the polymer define a *honeycomb-like* structure. A plasticizer, which typically has small molecules, intervenes to mask some of these attractions. The result is fewer points of attachment between polymer chains and a reduction in the rigidity of the structure.

In **polystyrene**, a benzene ring replaces one hydrogen atom in the polyethylene molecule. Because of the great bulk of such a ring, atactic polystyrene does not crystallize to any significant extent. The most familiar use of this polymer is in *polystyrene foam*, which is used in disposable containers for food and drinks and as insulation. A volatile liquid or a compound that dissociates to gaseous products on heating is added to the molten polystyrene. It forms bubbles that remain as the polymer is cooled and molded. The large number of gas-filled pockets in the final product make it a good thermal insulator. **Polyurethane** is another polymer that is fabricated as a *foam insulator*. It is made by the polymerization of a glycol with a *diisocyanate*, as in the reaction:



$$n\,\mathrm{HO{-}CH_2{-}CH_2{-}OH} + n\,\mathrm{O{=}C{=}N}\left[\mathrm{CH_2}\right]_m\mathrm{N{=}C{=}O} \longrightarrow \left[-\mathrm{O{-}CH_2{-}CH_2{-}O{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}\left[\mathrm{CH_2}\right]_m\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\right]_n$$

8.3.3 Rubber

An elastomer is a plastic that can be deformed to a large extent and still recover its original shape when the deforming stress is removed. The term **rubber** was introduced by Joseph Priestley, who observed that such materials can be used to rub out pencil marks. **Natural rubber**, the specific elastomer Priestley used, occurs in over 200 plant species. The only important source is the tropical rubber tree. When its bark is cut, this tree exudes latex, a milky fluid that contains about 35% natural rubber. Natural rubber is a polymer of **isoprene** (*2-methylbutadiene*). The isoprene molecule contains two double bonds, and polymerization removes only one of these, so natural rubber is unsaturated, containing one double bond per isoprene unit. In polymeric isoprene, the geometry at each double bond can be either *cis* or *trans*. Natural rubber is *all-cis polyisoprene*. The *all-trans form* also occurs in nature in the sap of certain trees. This material is used to cover golf balls because it is particularly tough. Isoprene can be polymerized by free-radical addition polymerization, but the resulting polymer contains a mixture of *cis* and *trans* double bonds and is useless as an elastomer.

Pure natural rubber has limited usefulness because it melts, is soft, and does not spring back fully to its original form after being stretched. In 1839 the American inventor Charles Goodyear discovered that if sulfur is added to rubber and the mixture is heated, the rubber becomes harder and more *resilient* and does not melt. This process is referred to as **vulcanization**. It involves the formation of sulfur bridges between the methyl side-groups on different chains. Small amounts of sulfur ($<5\%$) yield an elastic material in which sulfur links between chains remain after stretching and enable the rubber to regain its original form when the stretching force is removed. Large amounts give the very hard, non-elastic material *ebonite*.

Research on synthetic substitutes for natural rubber began in the United States and Europe before World War Ⅱ. An accidental discovery at the Du Pont Company led to the production of **neoprene**, a rubbery polymer formed from monomeric *chloroprene* (*2-chloro-1, 3-butadiene*), in which the methyl group on isoprene is replaced by chlorine. Further attention focused on copolymers of styrene with butadiene (now called SBR) and copolymers of acrylonitrile with butadiene (NBR). The Japanese occupation of the rubber-producing countries of Southeast Asia during World War Ⅱ sharply curtailed the supply of natural rubber to the Allied nations, and rapid steps were taken to increase production of **synthetic rubbers**. During those few years, many advances were made in production techniques, quantitative analysis, and basic understanding of rubber elasticity. Styrene-butadiene rubber production continued after the war, and in 1950 SBR exceeded natural rubber in overall production volume for the first time.

8.4 Polymer Nomenclature

Trivial names (frequently for natural polymers)

Source:	cellulose
Source and chemical property:	nucleic acid
Chemical action:	catalase
Main use:	starch

Poly(monomer) names— starting monomers (source-based)

***Disadvantage*:**

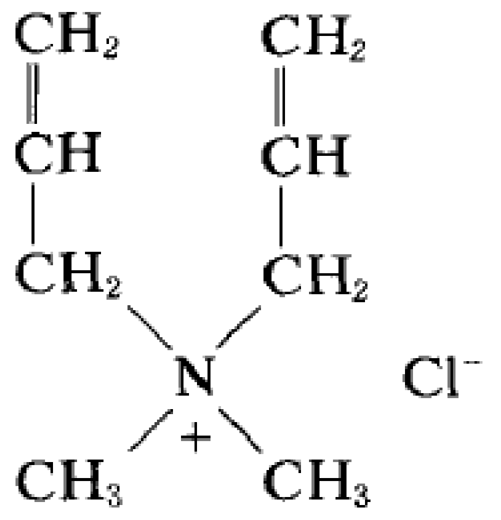
Constitution of the basic unit ≠ constitution of the monomers

Examples: **ethylene** → **poly(ethylene)**

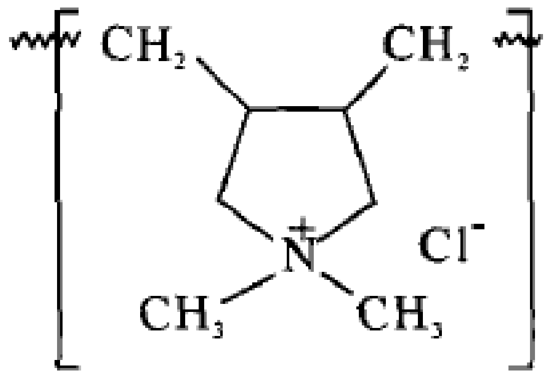
$CH_2=CH_2$ → $\sim(CH_2-CH_2)\sim$

The repetitive unit is methylene

DADMAC → **poly-DADMAC**



Diallyldimethylammonium chloride



The repetitive unit is 1,1-dimethyl-3,4-dimethylene-pyrrolidinium chloride

Polygroup names – refer to classes not to individual polymers (structure-based)

Examples:

polyamides: —NH—CO—

(diamines + dicarboxylic acids)

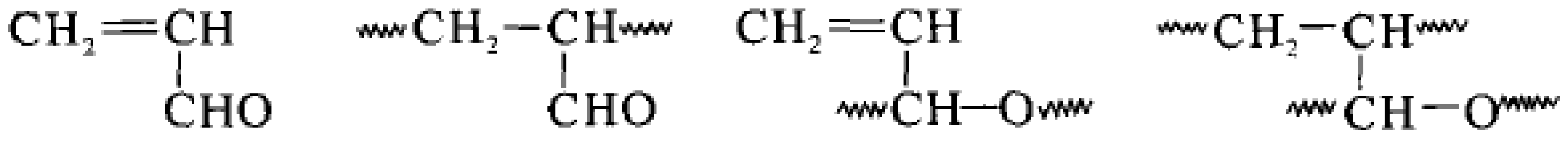
polyurethanes: —NH—CO—O—

polyesters: —CO—O—

***Disadvantage*:**

Fails, if more than one sort of basic unit result from one monomer

Examples:



$$\underset{\mathrm{CHO}}{\mathrm{CH_2{=}CH}} \qquad \sim\!\underset{\mathrm{CHO}}{\mathrm{CH_2{-}CH}}\!\sim \qquad \underset{\sim\mathrm{CH{-}O}\sim}{\mathrm{CH_2{=}CH}} \qquad \sim\!\underset{\sim\mathrm{CH{-}O}\sim}{\mathrm{CH_2{-}CH}}\!\sim$$

Acrolein **poly(acrolein)**

IUPAC Nomenclature (systematic names)

Combination of:

Principle of additivity (inorganic molecules)

Principle of substitution (organic molecules)

First step: Addition of the smallest repetition unit, intended to be a bivalent group (biradical)

– preferred constitutional unit –

Advantageous spelling: poly(...)

Examples:

Poly(methylene) $-CH_2-$ (written without spaces between words)

Second step: Designation of endgroups: α- ...-ω-...-poly(...)

Examples:

$Cl(CH_2)_nCCl_3$

α-chloro-ω-trichloromethyl-poly(methylene)

Examples for Trivial and Structural Names of Organic Macromolecules

Constitution	Trivial Name	Structural Name
$\sim CH_2 \sim$	poly(ethylene)	poly(methylene)
$\sim CH{=}CHCH_2CH_2\sim$	1,4-poly(butadiene)	poly(1-butenylene)
$\sim OCH_2\sim$	poly(formaldehyde)	poly(oxymethylene)
$\sim NHCH_2CH_2\sim$	poly(ethylenimine)	poly(iminoethylene)
$\sim COCH_2CH_2\sim$	poly(ethylene-co-carbon monoxide)	poly(1-oxotrimethylene)
$\sim O(CH_2)_2OOC(p-C_6H_4)CO\sim$	poly(ethyleneterephthalate)	poly(oxyethyleneoxyterephthaloyl)
$\sim CH(OH)—CH_2\sim$	poly(vinylalcohol)	poly(1-hydroxyethylene)
$OH\sim CH(CH_3)—CH_2\sim COOCH_3$	poly(methylmethacrylate)	poly[(1-methoxycarbonyl)-1-methyl-ethylene]

References

[1] David W Oxtoby, Wade A Freeman, Toby F Block. Chemistry: science of change: third edition [M]. Philadelphia: Saunders College Publishing, 1998.

[2] Rodriguez F, Cohen C, Ober C K, Archer L A. Principles of polymer systems: fifth edition [M]. New York: Taylor & Francis Books, 2003.

Chapter 9 New Materials

Material is anything made of matter, constituted of one or more substances. New materials have been among the greatest achievements of every age and they have been central to the growth, prosperity, security, and quality of life of humans since the beginning of history. It is always new materials that open the door to new technologies. Since the very beginning of the modern chemistry, a key goal of the chemical sciences is the creation of molecules and materials that do not exist in nature. Chemists have contributed to materials science by designing and synthesizing new substances and developing the means for processing naturally occurring and synthetic materials to form fibers, films, coatings, adhesives, and substances with special electrical, magnetic, or optical properties. In this chapter we will introduce several kinds of materials that play important roles in modern society.

9.1 Polymers

9.1.1 Liquid Crystalline Polymers

Liquid crystals (LCs) are a state of matter that have properties between those of a conventional liquid and those of a solid crystal. In the liquid crystal state, for molecules that are rod like, the rods can all line up with each other and order as in a solid crystal, but will also flow past each other as in a liquid. Thus, in a liquid crystal state molecules can orient to each other in the liquid state. This alignment of rod like molecules is what turns a **liquid crystalline display** (LCD) from dark to light in a calculator display (the alignment is turned on and off with an electric field). For other molecules, this alignment can occur automatically or can be caused by flow that occurs when a fiber or shape is formed.

Liquid-crystal polymers (**LCPs**) are a class of aromatic polyester polymers. Liquid crystallinity in polymers may occur either by dissolving a polymer in a solvent (**lyotropic liquid-crystal polymers**) or by heating a polymer above its glass or melting transition point (**thermotropic liquid-crystal polymers**). Liquid-crystal polymers are present in melted/liquid or solid form. In solid form the main example of lyotropic LCPs is the commercial aramid known as **Kevlar**. Chemical structure of this aramid consists of linearly substituted aromatic rings linked by amide groups. In a similar way, several series of thermotropic LCPs have been commercially produced by several companies (e.g., Vectra).

When liquid crystal polymers align themselves to each other, the molecules can often form connections or bonds between the rods, forming a two-dimensional, net-like structure that makes the fibers formed from these materials very strong. The most well-known of these materials, Kevlar™, was created in 1971. A young scientist at Du Pont, Stephanie Kwolek, became intrigued by the behavior of the liquid crystalline compound she was studying, *polyparaphenylene terephthalamide*. The molecules were long, straight and stiff; in addition, the molecules naturally oriented themselves into straight lines, with strong interchain bonding. The end result was a very symmetric and ordered structure, with the bonding between the rods creating an extremely reinforced **net-like structure**. Today, many products have evolved based on the natural properties of these liquid crystalline polymers.

A large number of LCPs, produced in the 1980s, displayed order in the melt phase analogous to that exhibited by nonpolymeric liquid crystals. Processing of LCPs from liquid-crystal phases (or **mesophases**) gives rise to fibers and injected materials having high mechanical properties as a consequence of the self-reinforcing properties derived from the macromolecular orientation in the mesophase.

Today, LCPs can be melt-processed on conventional equipment at high speeds with excellent replication of mold details. In fact, the high ease of forming of LCPs is an important competitive advantage against other plastics, as it offsets high raw material cost. LCP is a thermoplastic fiber with exceptional strength and rigidity (five times that of steel), and about 15 times the fatigue resistance of aramid.

It doesn't absorb moisture, has very low stretch, it doesn't creep like UHMW-PE fiber, and has excellent abrasion, wear, and chemical resistance. Its high **melting point** allows the retention of these properties over broad ranges of temperatures.

It is suitable for industrial, electronic, and aerospace applications, as well as for ropes and sport equipment.

Liquid crystalline polymers are also finding markets in other areas where its extraordinary strength can be very useful. For instance, another liquid crystalline polymer currently on the market (Vectran™) has double the stopping capacity of Kevlar™, and is finding applications in the sailing industry, as well as safety (airbags) and sports. So the basic science of these naturally reinforcing liquid crystals are the key to current high strength materials and, one hopes, future technological advances.

9.1.2 Dielectric Elastomers

A **dielectric** is an electrical insulator that may be polarized by the action of an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material, as in a conductor, but only slightly shift from their average equilibrium positions causing **dielectric polarization**: positive charges are displaced along the field and negative charges shift in the opposite direction. This creates an internal electric field which partly compensates the external field inside the dielectric. If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized, but also reorient so that their symmetry axis aligns to the field.

Recent experiments have shown that a voltage can induce a large deformation in an **elastomer** of **interpenetrating networks**. Dielectric elastomers (also called electrostrictive polymers) exhibit a **mechanical strain** when subjected to an electric field. Their striction capability is much higher than that of **piezoceramics** (10% - 30% vs. 0.1% - 0.3%).

Based on their simple working principle, **dielectric elastomer actuators (DEA)** transform electric energy directly into mechanical work. DEA are lightweight, have a high elastic energy density and are investigated since the late 90's. The most common DEA are PMMA-based electrostrictive polymers. Thanks to their electrostrictive strain, they can be sandwiched between two electrodes to emulate the operation of muscles. In an electric field, the elastomer expands in the plane of the electrodes, amplifying the normal compression due to the electrostatic charges on the electrodes. The result is a muscle with large strain capability, and a large actuation pressure.

Dielectric elastomers offer a wide variety of potential applications as a novel actuator technology that can replace many electromagnetic actuators, pneumatics, and piezó actuators. And dielectric elastomers can enable actuators to be integrated into applications that were previously infeasible.

9.1.3 Conductive Polymers

Conductive polymers are organic polymers that conduct electricity. Such compounds may be true metallic conductors or semiconductors. It is generally accepted that metals conduct electricity well and that organic compounds are insulating, but this class of materials combines the properties of both. The biggest advantage of conductive polymers is their **processability**. Conductive polymers are also plastics (which are organic polymers) and therefore can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. Their properties can be fine-tuned using the methods of organic synthesis.

Well-studied classes of organic conductive polymers include poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, polyanilines, poly(p-phenylene sulfide), and poly(p-phenylene vinylene)s (PPV). PPV and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity. The extended systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and the optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and the optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state.

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are often salt-like, which diminishes their solubility in organic solvents and hence their **processability**. Furthermore, the charged organic backbone is often unstable towards atmospheric **moisture**. Compared to metals, organic conductors can be expensive requiring multi-step synthesis. The poor processability for many polymers requires the introduction of solubilizing substituents, which can further complicate the synthesis.

9.1.4 Polymeric Sealing Materials

Sealing material is a type of substance used to seal joints or fill cracks in a porous surface. High demands are made on sealing materials to guarantee reliable sealing in constructions—both in new constructions and in repair works. Silicone (polysiloxane) is the elastomer of choice for a broad range of high-performance seals. It is **flexible** at low temperatures, has outstanding **heat resistance**, low compression set, and is a good electrical insulator.

Silicone maintains rubberlike properties through a wide range of temperatures, performing for extended periods at −150 to 500 °F. Actual service life at a given temperature varies with demands such as continuous flexing or shrinkage restrictions.

It generally does not have high **tensile strength**. However, silicone retains much of its inherent tensile strength at high temperatures. The material resists radiation, ozone and other gases, water, sunlight, oxidation, and is color stable. In fact, silicone seals exposed to outdoor weather for more than 15 years often show no significant loss of physical properties.

It can also be easily formulated to be either conductive or nonconductive. And, when properly fabricated, silicone does not stain, corrode, or in any way damage the materials it contacts.

Conventional silicones are classified as slow burning. They contain **non-halogen** flame retardants that do not produce corrosive or toxic by products. Consequently, they generate significantly less smoke during **combustion** than that given off by most organic elastomers.

Pound for pound, silicone tends to be pricier than many other sealing materials. But longer service life, along with less maintenance and repair over the seal's life span, frequently makes silicone rubber lower in total cost than competing materials.

However, it is not suited for applications that require abrasion, tear, and cut-growth resistance, or high-tensile strength. It is also not recommended for exposure to oil, gasoline, solvents, alkalis and acids. Fluoroelastomer-coated silicone, EPDM (Ethylene-Propylene-Diene Monomer), and nitrile can overcome these limitations.

Fluoroelastomers provide premium performance and long-term reliability in harsh and corrosive environments. Their exceptional resistance to heat, aging, and a broad range of fuels, solvents, and chemicals makes them ideal for many demanding aerospace, automotive, and industrial applications. Fluoroelastomers also offer excellent resistance to weather, ozone, oxygen, and sunlight, and are inherently more flame retardant than hydrocarbon rubbers.

On the downside, they tend to be among the most-expensive sealing materials. And **fluoroelastomers** have poor resistance to ketones, esters, ethers, amines, and aqueous bases such as ammonia and sodium hydroxide.

SBR (styrene-butadiene rubber) has excellent impact strength, good **resilience**, tensile strength, and abrasion resistance, and stays flexible at low temperatures. However, it is not the polymer of choice for applications requiring resistance to oil, gasoline, and hydrocarbon solvents. SBR is also unsuitable for exposure to the outside elements, such as UV and ozone. In addition to seals and gaskets, SBR can be found in tire treads, conveyor belt covers, mats, and even shoe soles.

9.1.5 Polymeric Stealth Material

Stealth is achieved mostly through the use of a polymer coating that is a near perfect absorber in typical radar wavelengths. **Radar absorbent material**, or RAM, is a class of materials used in stealth technology to disguise a vehicle or structure from radar detection. A material's **absorbency** at a given frequency of radar wave depends upon its composition. A radar absorbent material can significantly reduce an object's radar cross section in specific radar frequencies, but it does not result in "invisibility" on any frequency. The earliest forms of RAM were the materials called Sumpf and Schornsteinfeger, a coating used by Germans during the World War Ⅱ for the snorkels (or periscopes) of submarines, to lower their reflectivity in the 20-centimeter radar band the Allies used. The material had a layered structure and was based on graphite particles and other semiconductive materials embedded in a rubber matrix. The material's efficiency was partially reduced by the action of sea water.

Another similar "skin" is being tested at the top-secret Groom Lake facility at Area 51 in Nevada. It is reputed to be composed of an "electro-magnetically conductive polyaniline-based radar-absorbent composite material". The system also utilizes **photo-sensitive** receptors all over the plane that scan the surrounding area, subsequently the data is interpreted by an onboard computer which outputs it much like a computer screen making the aircraft virtually invisible to site.

Polypyrrole is used in microwave-absorbing "stealth" screen coatings and in sensing devices. Foam absorber is used as lining of anechoic chambers for electromagnetic radiation measurements. This material typically consists of fire proofed urethane foam loaded with carbon black, and cut into long pyramids. The length from base to tip of the pyramid structure is chosen based on the lowest expected frequency and the amount of absorption required. For low frequency damping, this distance is often 24 inches, while high frequency panels are as short as 3 – 4 inches. Panels of RAM are installed with the tips pointing inward to the chamber. Pyramidal RAM attenuates signal by two effects: **scattering** and **absorption**. Scattering can occur both coherently, when reflected waves are in-phase but directed away from the receiver, and incoherently where waves are picked up by the receiver but are out of phase and thus have lower signal strength. This incoherent scattering also occurs within the foam structure, with the suspended carbon particles promoting destructive interference. Internal scattering can result in as much as 10 dB of attenuation. Meanwhile, the pyramid shapes are cut at angles that maximize the number of bounces a wave makes within the structure. With each bounce, the wave loses energy to the foam material and thus exits with lower signal strength. Other foam absorbers are available in flat sheets, using an increasing gradient of carbon loadings in different layers.

9.1.6 Biopolymers

Biopolymers are polymers that are biodegradable. The input materials for the production of these polymers may be either renewable (based on agricultural plant or animal products) or synthetic. There are four main types of biopolymer based respectively on: starch, sugar, cellulose, and synthetic materials.

Current and future developments in biodegradable polymers and renewable input materials focus relate mainly to the scaling-up of production and improvement of product properties. Larger scale production will increase availability and reduce prices.

A major but defining difference between polymers and biopolymers can be found in their structures. Polymers, including biopolymers, are made of repetitive units called monomers. Biopolymers often have a well-defined structure, though this is not a defining characteristic (example: **ligno-cellulose**). The exact chemical composition and the sequence in which these units are arranged is called the primary structure, in the case of proteins. Many biopolymers spontaneously fold into characteristic compact shapes, which determine their biological functions and depend in a complicated way on their primary structures. Structural biology is the study of the structural properties of the biopolymers. In contrast most synthetic polymers have much simpler and more random (or **stochastic**) structures. This fact leads to a molecular mass distribution that is missing in biopolymers. In fact, as their synthesis is controlled by a template directed process in most in vivo systems all biopolymers of a type (say one specific protein) are all alike: they all contain the similar sequences and the numbers of monomers and thus all have the same mass. This phenomenon is called **monodispersity** in contrast to the **polydispersity** encountered in synthetic polymers. As a result biopolymers have a

polydispersity index of 1.

Besides being available on a sustainable basis, biopolymers have several economic and environmental advantages. Biopolymers could also prove an asset to waste processing. For example, replacing the polyethylene used in coated papers by a biopolymer could help eliminate plastic scraps occurring in compost.

The major advantage of biodegradable packaging is that it can be composted. But the **biodegradability** of raw materials does not necessarily mean that the product or package made from them (e. g. coated paper) is itself compostable.

Widespread interest for biopolymers is among consumers. Conventional plastics are environmentally unfriendly in the public perception. Sustainability can provide an image benefit. The environmental benefits of biodegradable packaging must be reflected in cost advantages, if large-scale applications are to become feasible. In the short term, it would be preferable to communicate the functional advantages of biodegradable packaging rather than its compostability.

9.1.7 Polymeric Membrane for Separation

Gas mixtures can be effectively separated by synthetic membranes. In the past several decades, membrane separation has gone from a laboratory curiosity to commercial reality. These membranes often have a separating layer thickness <100 nm and offer specific advantages in low energy costs, ease of operation, and compactness. Gas separation using polymeric membranes include many of the common gas pairs (i. e. O_2/N_2; H_2/N_2; CO_2/CH_4) in a multiplicity of applications.

Membrane separation of CO_2 from other gases is an active field, but the best membranes today are likely too energy intensive and expensive to be implemented on a large scale. Gas separation in membranes is driven by a pressure difference on either side of the membrane. Decreasing the required pressure difference by increasing the permeability of the membrane would reduce energy costs and required membrane area.

However, in order to obtain a sufficiently pure stream of CO_2, the selectivity for CO_2 must also be high. Many current systems require cascading the permeation through multiple membrane stages to achieve the desired purity.

Two areas of gas separation membrane research are polymer and inorganic membranes. Polymer membranes are relatively easy to manufacture and are suited for low temperature applications. The polymer **morphology** and mobility determine the gas permeability and selectivity.

Usually **nonporous polymeric membranes** are used. There, vapors and gases are separated due to their different solubility and diffusivity in polymers. Polymers in glassy state, generally more effective for separation, predominantly differentiate in diffusivity. Small molecules of penetrants move among polymer chains according to the formation of local gaps by thermal motion of polymer segments. Free volume of the polymer, its distribution and local changes of distribution are of the utmost importance. Then diffusivity of a penetrant depends mainly on the size of its molecule.

Porous membranes can also be utilized for the gas separation. The pores diameter must be smaller than the mean free path of gas molecules. Under normal condition (100 kPa, 300 K) it is about 50 nm. Then the gas flux through the pore is proportional to molecules velocity i.e. inversely proportional to square root of the molecule mass. It is known as **Knudsen diffusion**. Gas flux through a porous membrane is much higher than through nonporous one − 3 to 5 orders of magnitude. Separation efficiency is moderate − hydrogen passes 4 times faster than oxygen. Porous polymeric or ceramic membranes for ultrafiltration serve the purpose. Note, in case the pores are larger than the limit then viscous flow occurs, hence no separation.

9.2 Ceramics

9.2.1 Functional Glass

The properties of glass material allow a wide field of applications, from the high scale diffusion materials (windows bottles...) to very high-cost ones (jewels, optical filters...). For most of these applications, surface treatments increase the performances and enlarge the functions of base glass: lowemissivity, marking, self-cleaning or electrochromic functions for windows, functional or decorative applications in luxury and optics industries (interferential optical filters).

Self-cleaning glass is a specific type of glass with a surface which keeps itself free of dirt and grime through **photocatalytic decomposition**. The first self-cleaning glass was based on a thin film titanium dioxide coating. The glass cleans itself in two stages. The "**photocatalytic**" stage of the process breaks down the organic dirt on the glass using ultraviolet light and makes the glass **hydrophilic** (normally glass is **hydrophobic**). In a photocatalytic process, ultraviolet (UV) light from the sun energizes the SunClean glass coating to help slowly break down and loosen organic dirt. During the following "hydrophilic" stage, the coating's hydrophilic property makes water droplets spread out, or sheet, across the surface of the glass. Because of this, when rain or a light spray of water hits the window, the water helps to more effectively rinse away loosened dirt.

Titanium dioxide is a material of choice because it is characterized by high **photocatalytic** properties, chemical stability and low price. Its anatase phase is most photocatalytic. What is more, under the UV irradiation its surface structure changes to generate OH groups, making it **superhydrophilic**.

It is speculated that other possible application areas of self-cleaning glass are computer monitors and PDA screens, where fingerprints are undesirable.

Titanium dioxide-based glass cannot decompose thick non-transparent deposits, such as paint or silicone, waterstop fingerprints or bleeding after weathering, or stucco dust produced during construction.

Another approach to self-cleaning glass has been suggested, based on the hydrophobic "lotus effect".

9.2.2 Ceramic Superconductor

Although ceramics were historically thought of as insulating materials, ceramic superconductors were discovered in 1986. Some fine ceramics have been observed to exhibit superconductivity at significantly higher temperatures, up to about −140℃. The new ceramic superconductors usually contain copper oxide planes such as $YBa_2Cu_3O_7$ discovered in 1987 with $T_c = 93$ K.

They have **critical temperatures** above the boiling point of liquid nitrogen (77.4 K), which makes many potential applications of superconductors much more practical. This is due to the lower cost of liquid nitrogen and the easier design of cryogenic devices.

In addition to their critical temperature, two other parameters define the region where a ceramic material is superconducting: (1) the **critical current** and (2) the **critical magnetic field**. As long as the conditions are within the critical parameters of temperature, current, and magnetic field, the material behaves as a superconductor. If any of these values is exceeded, superconductivity is destroyed.

Applications of superconductors which rely on their current carrying ability include electrical power generation, storage and distribution. **SQUIDS** (Superconducting Quantum Interference Devices) are electronic devices that use superconductors as sensitive detectors of electromagnetic radiation. Possible applications in the field of medicine include the development of advanced **MRI** (Magnetic Resonance Imaging) units based on magnets made of superconducting coils.

9.2.3 Conductive Ceramics

Fine Ceramics are insulating materials in general, but some varieties exhibit electrical conductivity according to changes in temperature.

For ceramics, factors such as internal **porosity**, grain boundaries and impurities can affect this property. Higher or lower levels of thermal conductivity can be attained in Fine Ceramic materials by controlling these factors.

The property that measures how well heat is transmitted through a material is called thermal conductivity. Among Fine Ceramics, some materials possess high levels of conductivity and transfer heat well, while others possess low levels of conductivity and transfer less heat. A thermistor is an electronic component utilizing a property in which electrical resistance decreases as temperature increases, allowing electricity to flow more easily when the material gets hot. These devices are used in sensors that monitor temperature changes and in equipment designed to prevent electronics from overheating. A varistor is a similar component that possesses a property in which resistance decreases as voltage increases. Varistors are used to protect electronic circuits from excessive voltages.

Aluminum nitride and silicon carbide transfer heat particularly well. Aluminum nitride is used in packages for semiconductors that emit high volumes of heat, but must avoid accumulating heat internally. Zirconia blocks heat effectively and its coefficient of thermal conductivity is low — $\frac{1}{10}$ that of stainless steel. It is used for kiln walls, which are exposed to high temperatures. Materials with high thermal conductivity are used such as integrated circuit(IC) packages; materials with low thermal conductivity, such as kiln walls.

9.2.4 Piezoelectric Ceramics

Piezoelectric substances are polycrystalline materials consisting of lead zirconate titanate, or PZT. Lead (Pb), zirconium (Zr) and titanium (Ti) are combined with additives to achieve desired levels of performance. A PZT component possesses the unique ability to generate **vibrations** based on its shape when electricity is applied, and to generate electricity upon exposure to mechanical vibration or shock.

These are part of a class known as "smart" materials which are often used as sensors. Piezoelectric materials exhibit both a **direct** and a **reverse piezoelectric effect**. The direct effect produces an electrical charge when a mechanical vibration or shock is applied to the material, while the reverse effect creates a mechanical vibration or shock when electricity is applied.

This property can be tailored by means of the chemical composition, and is the basis for many commercial applications. These range from chemical sensors to large scale electric power generators. One of the most prominent technologies is that of fuel cells. It is based on the ability of certain ceramics to permit the passage of oxygen anions, while at the same time being electronic insulators. Zirconia (ZrO_2), stabilized with calcia (CaO), is an example of such a solid electrolyte.

Another example is the stovetop burner used in a typical kitchen gas range that is ignited by converting mechanical shock into an electrical arc that lights the gas. The clicking noise you hear when you turn the control dial is the sound of a piezoelectric ceramic being struck to induce the necessary mechanical shock. Some lighters also use this mechanism.

9.2.5 Magnetic Ceramics

Ferrite is well known among Fine Ceramic materials for its magnetic properties. Ferrites are made by mixing and sintering iron oxide, manganese oxide and nickel oxide powders. Their primary uses include serving as magnets and magnetic coils in a wide variety of electronic circuits, and in electronic devices, such as transformers and loudspeakers.

Ferrites are usually non-conductive **ferrimagnetic** ceramic compounds derived from iron oxides such as **hematite** (Fe_2O_3) or **magnetite** (Fe_3O_4) as well as oxides of other metals. Ferrites are, like most other ceramics, hard and brittle. In terms of the magnetic properties, ferrites are often classified as "soft" and "hard" which refers to their low or high **coercivity** of their magnetism, respectively.

Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, and/or manganese compounds. They have a low coercivity and are called soft ferrites. The low coercivity means the material's magnetization can easily reverse direction without dissipating much energy (**hysteresis losses**), while the material's high resistivity prevents eddy currents in the core, another source of energy loss. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of RF transformers and inductors in applications such as switched-mode power supplies (SMPS).

The most common soft ferrites are manganese-zinc (MnZn, with the formula $Mn_a Zn_{(1-a)} Fe_2 O_4$) and nickel-zinc (NiZn, with the formula $Ni_a Zn_{(1-a)} Fe_2 O_4$). NiZn ferrites exhibit higher resistivity than MnZn, and are therefore more suitable for frequencies above 1 MHz. MnZn have in comparison higher permeability and saturation induction.

In contrast, permanent ferrite magnets are made of hard ferrites, which have a high coercivity and high remanence after magnetization. These are composed of iron and barium or strontium oxides. In a magnetically **saturated state** they conduct magnetic flux well and have a high magnetic permeability.

This enables these so-called ceramic magnets to store stronger magnetic fields than iron itself. They are cheap, and are widely used in household products such as refrigerator magnets. The maximum magnetic field B is about 0.35 tesla and the magnetic field strength H is about 30 to 160 kiloampere turns per meter (400 to 2000 oersteds).

9.2.6 Bioceramics

Ceramic materials that are specially developed for use as medical and dental implants are termed bioceramics. Bioceramics are an important subset of biomaterials. They include alumina and zirconia, **bioactive** glasses, glass-ceramics, coatings and composites, hydroxyapatite and resorbable calcium phosphates, and **radiotherapy** glasses.

The thermal and the chemical stability of ceramics, high strength, wear resistance and durability all contribute to making ceramics good candidate materials for surgical implants.

Ceramics in a number of forms and compositions are currently in use or under consideration, with more in development. Alumina and zirconia are among the **bioinert** ceramics used for prosthetic devices. Bioactive glasses and machinable glass-ceramics are available under a number of trade names. Porous ceramics such as calcium phosphate-based materials are used for filling bone defects. The ability to control porosity and solubility of some ceramic materials offers the possibility of use as drug delivery systems. One proposed use for bioceramics is the treatment of cancer. Two methods of treatment have been proposed; treatment through **hyperthermia**, and radiotherapy. Hyperthermia treatment involves implanting a bioceramic material which contains a ferrite or other magnetic material. The area is then exposed to alternating magnetic field which causes the implant and the surrounding area to heat up. Alternatively the bioceramic materials can be doped with β-emitting materials and implanted into the cancerous area.

Bioceramics can have structural functions as joint or tissue replacements, can be used as coatings to improve the **biocompatibility** of metal implants, and can function as resorbable lattices which provide temporary structures and a framework that is dissolved, replaced as the body rebuilds tissue. Some ceramics even feature drug-delivery capability.

9.3 Metallic Materials

9.3.1 Shape Memory Materials

A shape memory alloy (SMA) is an alloy that "remembers" its original, cold-forged shape when heated above a certain transition temperature. For example, a spring made of memory alloy can be stretched in the hot water and can shrink to the original size in cold water with itself by unlimited times. The reason for its shape memory effect is the existence of relatively stable structure states under different temperatures. One of the most common SMA is the nickel-titanium (NiTi) alloy. Since the crystal structure of NiTi alloy at a temperature lower than 40 ℃ is different from that at a temperature higher than 40 ℃, it changes its shape around 40 ℃. Thus, 40 ℃ is the **key temperature point** of NiTi alloy. Different memory alloys have different key temperature points.

Shape memory alloys have different shape memory effects. Two common effects are one-way and two-way shape memory. **One-way memory effect**: when a shape memory alloy is in its cold state, the metal can be bent or stretched and will hold those shapes until heated above the transition temperature. Upon heating, the shape changes to its original. When the metal cools again it will remain in the hot shape, until deformed again. The **two-way shape memory effect** is the effect that the material remembers two different shapes: one at low temperatures, and the other at the high temperature shape. A material that shows a shape memory effect during both heating and cooling is called two-way shape memory. This can also be obtained without the application of an external force (intrinsic two-way effect).

The procedures, as shown in Figure 9.1, are very similar: starting from **martensite** (a) adding a reversible deformation for the one-way effect or severe deformation with an irreversible amount for the two-way, (b) heating the sample (c) and cooling it again (d).

Recently, Ti-Ni based, brass based and iron-based memory alloy have

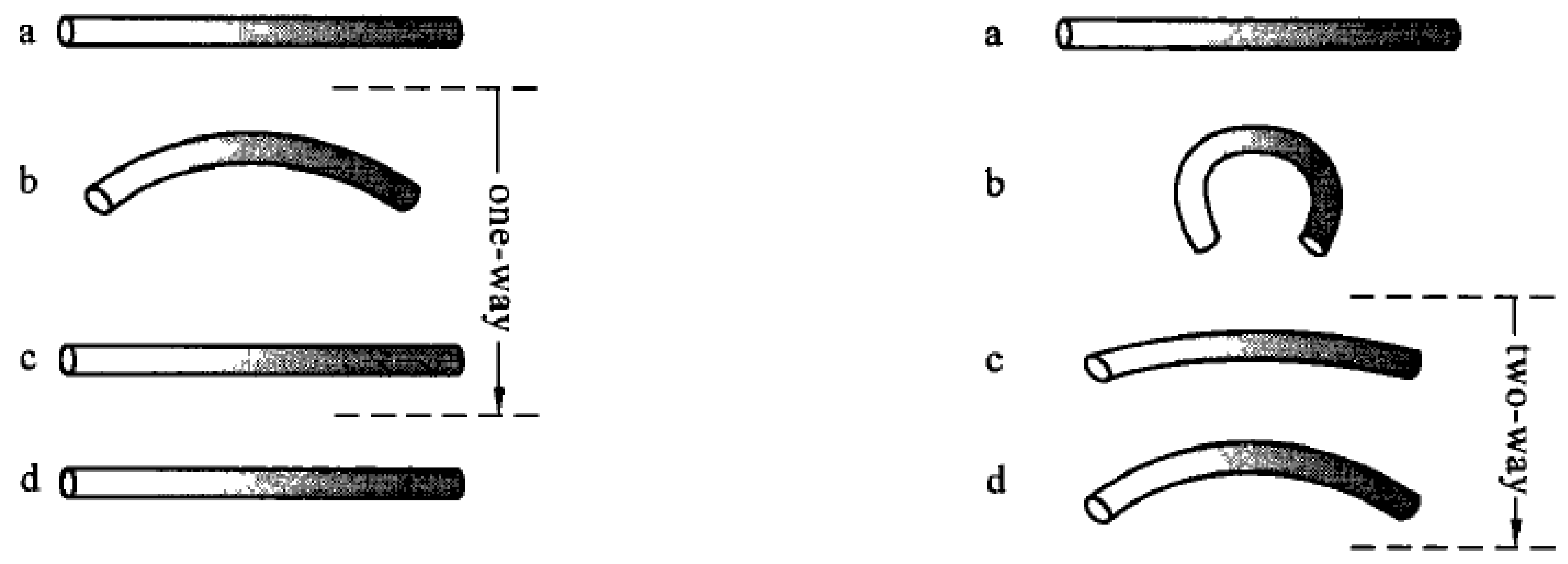


Figure 9.1 Skematical representation of recovery for different shape memory metals

been under investigations.

Some applications of memory alloy are as follows:

(1)single way memory, such as pipe tie-in, antenna, lantern ringer etc;

(2)double way memory, by outside force, repeated motion of material with the temperature modification using the single way memory;

(3) super stretch application, such as spring, glass frame, connection pole;

(4)iatrical application for biological consistency as thrombus filter, spine rectifier, artificial joint etc.

9.3.2 Amorphous Metal

An **amorphous metal** is a metallic material with a disordered atomic-scale structure. In contrast to most metals, which are crystalline and therefore have a highly ordered arrangement of atoms, amorphous alloys are non-crystalline. Materials in which such a disordered structure is produced directly from the liquid state during cooling are called "glasses", and so amorphous metals are commonly referred to as "**metallic glasses**" or "**glassy metals**". However, there are several other ways in which amorphous metals can be produced, including *physical vapor deposition*, *solid-state reaction*, *ion irradiation*, *melt spinning*, and *mechanical alloying*. Amorphous metals produced by these techniques are, strictly speaking, not glasses. However, materials scientists commonly consider amorphous alloys to be a single class of materials, regardless of how they are prepared.

In the past, small batches of amorphous metals have been produced through a variety of quick-cooling methods. For instance, amorphous metal wires have been produced by sputtering molten metal onto a spinning metal disk. The rapid cooling, on the order of millions of degrees a second, is too fast for crystals to form and the material is "locked in" a glassy state. More recently a number of alloys with critical cooling rates low enough to allow formation of amorphous structure in thick layers (over 1 millimeter) had been produced; these are known as **bulk metallic glasses** (**BMG**). More recently, batches of amorphous steel have been produced that demonstrate strengths much greater than conventional steel alloys.

Amorphous metal is usually an alloy rather than a pure metal. The alloys contain atoms of significantly different sizes, leading to low free volume (and therefore up to orders of magnitude higher viscosity than other metals and alloys) in molten state. The viscosity prevents the atoms moving enough to form an ordered lattice. The material structure also results in low shrinkage during cooling and resistance to **plastic deformation**. The absence of grain boundaries, the weak spots of crystalline materials, leads to better resistance to wear and corrosion. Amorphous metals are also much tougher and less brittle than oxide glasses and ceramics. Thermal conductivity of amorphous materials is lower than that of crystals. Amorphous metals exhibit unique softening behavior above their glass transition and this softening has been increasingly explored for thermoplastic forming of metallic glasses.

It has been shown that metallic glasses can be patterned on extremely small length scales ranging from 10 nm to several millimeters. It has been suggested that this may solve the problems of **nanoimprint lithography** where expensive nano-molds made of silicon break easily. Nano-molds made from metallic glasses are easy to fabricate and more durable than silicon molds.

9.3.3 Hydrogen Storage Alloy

Hydrogen storage alloys are metallic materials that have a unique ability to absorb and hold large amounts of hydrogen by bonding with hydrogen and forming hydrides. A hydrogen storage alloy is capable of absorbing and releasing hydrogen without compromising its own structure.

The hydrogen storage alloys in common use occur in four different forms: AB_5(e.g., $LaNi_5$), AB (e.g., FeTi), A_2B (e.g., Mg_2Ni) and AB_2 (e.g., ZrV_2). Among them, the AB_5 and the AB_2 type alloys have the most advantageous combination of high hydrogen storage capacities and operations parameters.

The AB_5 alloys combine a hydride forming metal A, usually a rare earth metal (La, Ce, Nd, Pr, Y or their mixture known as Mischmetal), with a non-hydride forming element - nickel. The latter can be doped with other metals, such as Co, Sn or Al, to improve material's stability or to adjust equilibrium hydrogen pressure and temperature required for its charging discharging with hydrogen.

The AB_2 alloys, also known as **Laves phases**, represent a large group of alloys containing titanium, zirconium or hafnium at the A site and a transition metal(s) at a B site (Mn, Ni, Cr, V and others). Reversible hydrogen storage capacities of this group of materials are comparable with those of the AB_5 type alloys. However, AB_2 alloys are capable of storing additional amounts of hydrogen at high hydrogen pressures and have higher capacities at high discharge rates when used as negative electrodes in batteries. Due to reasonably high hydrogen storage capacities (1.4wt%~1.6 wt%) and consistent performance, the AB_5 and the AB_2 type alloys can serve as excellent reference materials in hydrogen absorption and desorption experiments using gas-sorption systems.

They are typically used in portable computers and in electronics, cell phones and power tools. They are also being used in the newly emerging hybrid vehicles. These batteries both supply energy to and draw energy from the gas-powered motor, eliminating the need for a separate recharging.

Hydrogen storage alloys can be used to purify hydrogen because they absorb the three **isotopes** of hydrogen (protium, deuterium and tritium) at different rates.

Another property of hydrogen storage alloys is that they release heat when absorbing hydrogen and absorb heat when releasing hydrogen. This property allows their use in heat pumps, heaters and air conditioners. In a heat pump, two hydride beds containing the same type of alloy are connected by a compressor. The compressor drives the hydrogen from one bed to the second bed, causing cooling at the first bed and heating at the second bed. These alloys can also be used to power compressors. Compressors make use of the reverse activity that heat pumps do: changing the alloy's temperature creates a change in pressure as it absorbs/releases hydrogen, creating enough force to do work.

This is also the theory behind temperature sensor-actuators, which utilize the force generated by a release in pressure when the temperature increases. When the hydrogen storage alloys in these mechanisms are activated by a temperature increase, they generate enough force to open or close valves, as demonstrated by a fire sprinkler that turns water on when it detects a fire, and off again as it cools.

9.3.4 Superconducting Materials

Superconductivity occurs in certain materials at very low temperatures. When superconductive, a material has an electrical resistance of exactly zero. It was discovered by Heike Kamerlingh Onnes in 1911. Like *ferromagnetism* and *atomic spectral lines*, superconductivity is a *quantum mechanical phenomenon*. It is also characterized by a phenomenon called the **Meissner effect**. This is the ejection of any sufficiently weak magnetic field from the interior of the superconductor as it transitions into the superconducting state. The presence of the Meissner effect indicates that superconductivity cannot be understood simply as the idealization of "perfect conductivity" in classical physics.

The electrical resistivity of a metallic conductor decreases gradually as the temperature is lowered. However, in ordinary conductors such as copper and silver, this decrease is limited by impurities and other defects. Even near absolute zero, a real sample of copper shows some resistance. In a superconductor however, despite these imperfections, the resistance drops abruptly to zero when the material is cooled below its critical temperature. An electric current flowing in a loop of superconducting wire can persist indefinitely with no power source.

Superconductivity occurs in many materials: simple elements like tin and aluminium, various metallic alloys and some heavily-doped semiconductors. Superconductivity does not occur in noble metals like gold and silver, nor in pure samples of ferromagnetic metals.

The applications for superconducting materials fall into two general categories: electronics and magnets. All electronic devices will operate more efficiently if they are made from superconducting materials rather than from ordinary conducting materials. However, given the fact that those materials have to be kept at the temperature of liquid nitrogen, those applications have only a limited commercial application so far.

9.3.5 Nanocrystalline Metals

Researchers at Purdue University have made a surprising discovery that could open up numerous applications for metal "**nanocrystals**", or tiny crystals that are often harder, stronger and more wear resistant than the same materials in bulk form.

The thermomechanical characteristics of metals and alloys can be improved by controlling the nano-/microstructure of the materials. Melting points and sintering temperatures can be reduced up to 30%, if the material is made of nanopowders. Another advantage is the easy formability of the materials through **superplasticity**.

Nanocrystals of various metals have been shown to be 100%, 200% and even as much as 300% harder than the same materials in bulk form. Because wear resistance often is dictated by the hardness of a metal, parts made from nanocrystals might last significantly longer than conventional parts.

References

[1] George K, Mayo I. Memory metal [J]. Chem Matters, 1993: 4-7.

[2] Roya R, Majumdara AK. Thermomagnetic and transport properties of metglas 2605 SC and 2605 [J]. Journal of Magnetism and Magnetic Materials, 1981(25): 83 - 89.

[3] Ponnambalam V, Poon S J, Shiflet G J. Fe-based bulk metallic glasses with diameter thickness larger than one centimeter [J]. Journal of Materials Research, 2004(19): 1320-1326.

[4] Kumar G, Tang H, Schroers J. Nanomoulding with amorphous metals [J]. Nature, 2009(457): 868 - 872.

[5] http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Brochure/al_material_matters_v2n2.Par.0001.File.tmp/al_material_matters_v2n2.pdf.

[6] Liu X H, Wang X. Non - crystal multilayer diamond film material with metal titanium as interface layer and its preparing method and use[P]. Patent Publication Number: CN 1227162.

[7] Callister W D. Materials science and engineering - an introduction, seventh edition [M]. New York: John Wiley & Sons, 2007.

[8] Pelrine R, Kornbluh R, Pei Q B, Joseph J. High - speed electrically actuated elastomers with strain greater than 100% [J]. Science. 2000(287): 836 - 839.

[9] Naarmann H. "Polymers, electrically conducting" in Ullmann's encyclopedia of industrial chemistry [G]. Weinheim: Wiley - VCH, 2002.

[10] Heeger A J, Schrieffer J R, Su W P. Solitons in conducting polymers [J]. Reviews of Modern Physics, 1998 (60): 781 - 784.

[11] Smith T. Seal materials for protecting sign case electronics [J]. Anti - Corrosion Methods and Materials, 1993(32): 7.

[12] http://www.radarworld.org/radarwar.pdf.

[13] Robeson L M. Metallic glasses [J]. Current Opinion in Solid State and Materials Science, 1999(4):549 - 552.

[14] http://news.bbc.co.uk/2/hi/technology/3770353.stm.

[15] http://www.sciencedaily.com/releases/2005/01/050125085826.htm.

[16] http://www.britannica.com/EBchecked/topic/101633/cellulose.

[17] http://www.srs.gov/general/sci - tech/technologies/hydrogen/dsmh.html.

[18] http://www.sendai.kopas.co.jp/METAL/PUBS/thesis_j/j_abst/63 - 05/601 - 604.html.

[19] http://www.hydrides.com/.

[20] http://www.sciencedaily.com/releases/2001/06/010605071757.htm.

[21] http://www.scienceclarified.com/Sp - Th/Superconductor.html.

[22] http://en.wikipedia.org/wiki/Thin_film.

[23] http://www.azonano.com/details.asp? ArticleID = 1136 # _Nanocrystalline_Metals_and_Alloys%20 - .

[24] http://news.uns.purdue.edu/UNS/html4ever/020816.Chandrasekar.nano.html.

[25] http://www.factofthematter.net/articles/kevlar.html.

[26] http://www.designinsite.dk/htmsider/m0670.htm.

[27] http://www.designinsite.dk/htmsider/m1329.htm.

[28] http://machinedesign.com/article/seven - versatile - sealing - materials - 0208.

[29] http://www.chemistryexplained.com/Pl-Pr/Polymers-Synthetic.html.

[30] http://www.physicsforums.com/archive/index.php/t-31853.html.

[31] http://www.bbc.co.uk/dna/ww2/A591545.

[32] http://www.o2.org/ideas/cases/biopolymers.html.

[33] http://matsel.mse.uiuc.edu/ceramics/prin.html.

[34] http://global.kyocera.com/fcworld/charact/heat/thermalcond.html.

[35] http://global.kyocera.com/fcworld/charact/elect/conductive.html.

[36] http://global.kyocera.com/fcworld/charact/elect/piezo.html.

[37] http://www.csa.com/discoveryguides/archives/bceramics.php.

Appendix

Laboratory Glassware and Equipment

absorption bottle	吸收瓶
adapter	接头、接液管
addition funnel	加液漏斗
addition funnel with pressure-equalization arm	恒压漏斗
air condenser	空气冷凝管
analytical balance	分析天平
automatic titrator	自动滴定仪
balance	天平
beaker	烧杯
beaker brush	烧杯刷
beaker tong	烧杯钳
blast alcohol burner	酒精喷灯
boiling flask	烧瓶
boiling stone	沸石
bottle brush	试剂瓶刷
Buchner funnel	布氏漏斗
Buchner funnel with fritted disc	布氏砂心漏斗
Bunsen burner	本生灯、煤气灯
buret (burette)	滴定管
buret brush	滴定管刷
burette clamp	滴定管夹
burette stand	滴定架台
centrifuge	离心机
centrifuge tube	离心管
centrifuge tube brush	离心管刷
circulating water bath	循环水浴锅
Claisen distilling head	克氏蒸馏头
clay triangle	瓷三角
clip	夹、钳、回形针
cold finger	指形冷冻器、冷指
condenser	冷凝管
condenser-Allihn type	球形冷凝管
condenser-west tube	直形冷凝管
conical flask	三角瓶
cork	软木塞

crucible	坩埚
crucible cover	坩埚盖
crucible tong	坩埚钳
crystallizing dish	结晶皿
culture bottle	培养瓶
cuvette	比色皿、小杯
desiccator	干燥器、保干器
distilling adapter	蒸馏转接头
distilling apparatus	蒸馏装置
distilling flask	支管蒸馏烧瓶
distilling head	蒸馏头
distilling tube	蒸馏管
double-buret clamp	蝴蝶夹
drop funnel	滴液漏斗
dropper	滴管
dropping funnel	滴液漏斗
dry rack	滴水架
drying cabinet	干燥箱、烘箱
drying tube	干燥管
dust mask	口罩、防尘面具
Erlenmeyer flask	锥形瓶　爱伦美氏(烧)瓶
evaporating dish (porcelain)	(瓷)蒸发皿
extension clamp	万能夹
eyewash equipment	洗眼器
filter flask (suction flask)	抽滤瓶
filtering funnel	滤液漏斗
fire blanket	灭火毯
first aid pyxides	急救箱
flask	烧瓶
Florence flask	平底烧瓶
forcep	镊子
fractionating column	分馏柱
fractionating flask	分馏(烧)瓶
fume hood	通风橱
funnel	漏斗
gas washing bottle	洗气瓶
gauze	石棉网
Geiser burette (stopcock)	酸氏滴定管
glass cutter	玻璃刀
glass-stoppered bottle	玻璃塞瓶
globe-shaped funnel	球形分液漏斗

Gooch filtering crucible	砂心坩埚
graduated cylinder	量筒
graduated flask	量瓶
Graham condenser	蛇形冷凝管
ground-glass stoppered flask	磨口玻璃瓶
hammer	锤、榔头
heat insulation gloves	隔热手套
heating mantle	加热罩
Hirsch funnel	赫氏漏斗
hot plate	电热板
hygrothermometers	湿度计
iron support	铁架台
lab jack	升降台
lab spoon	药匙
Liebig condenser	李比希冷凝管、空气冷凝管
long-stem funnel	长颈漏斗
magnetic stir bar	搅拌磁子
magnetic stirrer	磁力搅拌器
measuring bottle	量瓶
measuring cylinder	量筒
microliter syringe	微量进样器
micrometer	千分尺
microscope	显微镜
microscope slide	显微镜载玻片
microtiter plate	微量滴定板
mohr burette for use with pinchcock	碱氏滴定管
mohr measuring pipette	量液管
mortar	研钵
Muffle furnace	马弗炉
narrow-mouth flask	细口烧瓶
narrow-necked bottle	细颈瓶
oven	烘箱
paper label	标签纸
pear shaped flask	梨形瓶
pear-shaped funnel	梨形分液漏斗
pestle	研杵
Petri dish	培养皿
pH indicator paper	pH 试纸
pinch clamp	弹簧节流夹
pipet (pipette)	移液管、吸移管
pipet rack	移液管架

pipette stand	移液管架
plastic beaker	塑料烧杯
plastic squeeze bottle	塑料洗瓶
platform balance	台秤、托盘天平
reagent bottle	试剂瓶、玻璃瓶
receiving flask	接收瓶、收集瓶
reducing bush	大变小转换接头
refrigerator	冰箱
respirator	口罩、防毒面具
retort clamp	蒸馏瓶夹
ring stand	铁架台
rotary evaporator	旋转蒸发器
round-bottom(ed) flask	圆底烧瓶
rubber pipette bulb	吸耳球
rubber stopper	橡胶塞
rubber tubing	橡胶管
safety spectacle	防护眼镜
sampler	取样器
sampling bottle	取样瓶
Schlenk flask	舒伦克烧瓶
scissor	剪刀
scoopula	勺、匙
screw clamp	螺旋夹
screw driver	螺丝刀(起子)、改锥
separating flask	分液瓶
separatory funnel	分液漏斗
short-necked flask	短颈瓶
short-stem funnel	短颈漏斗
side-tube flask	支管烧瓶
Soxhlet extraction apparatus	索氏抽提装置
Soxhlet extractor	索氏抽提器
spanner	扳手
spatula	药匙、刮刀
specific gravity bottle	比重瓶
spirit burner	酒精灯
stainless-steel beaker	不锈钢杯
stir rod	搅拌棒
stopcock	旋塞
stopper	塞子
stopper borer	打孔器
stopwatch	秒表

tap funnel	分液漏斗
test tube	试管
test tube holder	试管夹
test tube rack	试管架
three-necked flask	三口瓶
thermometer	温度计
Thiele melting point tube	提勒熔点管
transfer pipette	移液管
tripod	三脚架
tube brush	试管刷
tube funnel	管式漏斗、滤管
tube rack	试管架
ultra-filtration funnel	超滤漏斗
ultrasonic cleaner	超声波清洗机
vacuum [Dewar] flask	真空瓶、杜瓦(真空)瓶
vacuum adapter	真空接收管
vacuum pump	真空泵
vacuum-filtering flask	真空过滤瓶
vacuum-pressure desiccator	真空干燥器
vernier caliper	游尺、游标、游标尺
vial	小瓶、小玻璃瓶
volumetric cylinder	量筒
volumetric flask	容量瓶
volumetric flask brush	容量瓶刷
wash bottle	洗瓶
watch glass	表面皿
water-bath	水浴
weighing bottle	称量瓶
weighing paper	称量纸
wide-mouth bottle	广口瓶
wire coil for heater	电炉丝