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Викладено фундаментальні положення загальної, неорганічної і органічної хімії та проаналізовано реакційну здатність найважливіших класів неорганічних і органічних речовин. Запропоновано багатоваріантні завдання та вправи для аудиторної та самостійної роботи студентів. Розраховано на студентів вищих навчальних закладів денної та заочної форм навчання напрямів „Хімічні технології та інженерія", „Нафтогазова інженерія та технології" та ін.

Stated fundamental theoretical principles of general, inorganic and organic chemistry and analyzed the reactivity of the most important classes of inorganic and organic substances. A multivariate tasks and exercises for classroom and independent work are proposed. For university students full-time and distance learning areas "Chemical Technology and Engineering" "Oil and gas engineering and technology" and others.

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CONTENT

PREFACE

Having studied and taught chemistry for some years, we are well aware of the problems foreign students encounter. We also know that students don’t always read the preface, so we wanted to remind you of all the resources available to help you master inorganic and organic chemistry.

Each individual learns in a different way. We have incorporated a number of features into the text help you tailor a study program that meets your particular needs and learning style.

Problem solving is an important part of chemistry, and it only becomes easier with practice. We worked hard to create a consistent problem solving approach in each in-chapter example. Try the related exercise on your own, and use the corresponding end-of-chapter practice problems to gain mastery of your problem-solving skills.

We have put a lot of time and thought into how to help you succeed. The following guide highlights how to get the most from the features of your textbook, and we hope you take advantage of all the technology and resources available with general and organic chemistry. Best of luck in your study!

M. Ved
D. Alami
M. Slavkova

PART I INORGANIC CHEMISTRY

CHAPTER 1 Introduction to general chemistry: basic concepts about matter

1.1 Subject of chemistry. States and properties of matter

Chemistry is the field of study concerned with the characteristics, composition, and transformations of matter. Matter is anything that has mass and occupies space. The term mass refers to the amount of matter present in a sample.

Various forms of energy such as heat, light, and electricity are not considered to be matter. However, chemists must be concerned with energy as well as with matter because nearly all changes that matter undergoes involve the release or absorption of energy.

The scope of chemistry is extremely broad, and it touches every aspect of our lives. An iron gate rusting, a chocolate cake baking, the diagnosis and treatment of a heart attack, the propulsion of a jet airliner, and the digesting of food all fall within the realm of chemistry. The key to understanding such diverse processes is an understanding of the fundamental nature of matter, which is what we now consider.

Three physical states exist for matter: ***solid, liquid, and gas.*** The classification of a given matter sample in terms of physical state is based on whether its shape and volume are definite or indefinite.

Solid is the physical state characterized by a definite shape and a definite volume. A dollar coin has the same shape and volume whether it is placed in a large container or on a table top. For solids in powdered or granulated forms, such as sugar or salt, a quantity of the solid takes the shape of the portion of the container it occupies, but each individual particle has a definite shape and definite volume. ***Liquid*** is the physical state characterized by an indefinite shape and a definite volume. A liquid always takes the shape of its container to the extent that it fills the container. ***Gas*** is the physical state characterized by an indefinite shape and an indefinite volume. A gas always completely fills its container, adopting both the container's volume and its shape.

The state of matter observed for a particular substance depends on its temperature, the surrounding pressure, and the strength of the forces holding its structural particles together.

Various kinds of matter are distinguished from each other by their properties. ***A property*** is a distinguishing characteristic of a substance that is used in its identification and description. Each substance has a unique set of properties that distinguishes it from all other substances. Properties of matter are of two general types: physical and chemical.

A physical property is a characteristic of a substance that can be observed without changing the basic identity of the substance. Common physical properties include color, odor, physical state (solid, liquid, or gas), melting point, boiling point, and hardness.

A chemical property is a characteristic of a substance that describes the way the substance undergoes or resists change to form a new substance. When we specify chemical properties, we usually give conditions such as temperature and pressure because they influence the interactions between substances. For example, the gases oxygen and hydrogen are unreactive toward each other at room temperature, but they interact explosively at a temperature of several hundred degrees.

Changes in matter are common and familiar occurrences. Changes take place when food is digested, paper is burned, and a pencil is sharpened. Like properties of matter, changes in matter are classified into two categories: physical and chemical.

A physical change is a process in which a substance changes its physical appearance but not its chemical composition. A new substance is never formed as a result of a physical change. A change in physical state is the most common type of physical change. Melting, freezing, evaporation, and condensation are all changes of state. In any of these processes, the composition of the substance undergoing change remains the same even though its physical state and appearance change. The melting of ice does not produce a new substance; the substance is water both before and after the change. Similarly, the steam produced from boiling water is still water.

A chemical change is a process in which a substance undergoes a change in chemical composition. Chemical changes always involve conversion of the material or materials under consideration into one or more new substances, each of which has properties and composition distinctly different from those of the original materials. Consider, for example, the rusting of iron objects left exposed to moist air. The reddish brown substance (the rust) that forms is a new substance with chemical properties that are obviously different from those of the original iron.

1.2 Pure substances and mixtures

In addition to its classification by physical state, matter can also be classified in terms of its chemical composition as a pure substance or as a mixture. ***A pure substance*** is a single kind of matter that cannot be separated into other kinds of matter by any physical means. All samples of a pure substance contain only that substance and nothing else. Pure water is water and nothing else. Pure sucrose (table sugar) contains only that substance and nothing else.

A pure substance always has a definite and constant composition. This invariant composition dictates that the properties of a pure substance are always the same under a given set of conditions. Collectively, these definite and constant physical and chemical properties constitute the means by which we identify the pure substance.

A mixture is a physical combination of two or more pure substances in which each substance retains its own chemical identity. Components of a mixture retain their identity because they are physically mixed rather than chemically combined. Consider a mixture of small rock salt crystals and ordinary sand. Mixing these two substances changes neither the salt nor the sand in any way. The larger, colorless salt particles are easily distinguished from the smaller, light-gray sand granules.

One characteristic of any mixture is that its components can be separated by using physical means. In our salt-sand mixture, the larger salt crystals could be though very tediously "picked out" from the sand. A somewhat easier separation method would be to dissolve the salt in water, which would leave the undissolved sand behind. The salt could then be recovered by evaporation of the water. Another characteristic of a mixture is variable composition. Numerous different salt-sand mixtures, with compositions ranging from a slightly salty sand mixture to a slightly sandy salt mixture, could be made by varying the amounts of the two components.

Mixtures are subclassified as heterogeneous or homogeneous. This subclassification is based on visual recognition of the mixture's components. ***A heterogeneous mixture*** is a mixture that contains visibly different phases (parts), each of which has different properties. A nonuniform appearance is a characteristic of all heterogeneous mixtures. Naturally occurring heterogeneous mixtures include rocks, soils, and wood. ***A homogeneous mixture*** is a mixture that contains only one visibly distinct phase (part), which has uniform properties throughout. The components present in a homogeneous mixture cannot be visually distinguished. A sugar-water mixture in which all of the sugar has dissolved has an appearance similar to that of pure water. Air is a homogeneous mixture of gases; motor oil and gasoline are multicomponent homogeneous mixtures of liquids; and metal alloys such as 14-karat gold (a mixture of copper and gold) are examples of homogeneous mixtures of solids. The homogeneity present in solid-state metallic alloys is achieved by mixing the metals while they are in the molten state.

1.3 Elements and compounds. Properties of atoms and molecules

Chemists have isolated and characterized an estimated 9 million pure substances. A very small number of these pure substances are different from all of the others. They are elements. All of the rest, the remaining millions, are compounds. What distinguishes an element from a compound?

An element is a pure substance that cannot be broken down into simpler pure substances by chemical means such as a chemical reaction, an electric current, heat, or a beam of light. The metals gold, silver, and copper are all elements.

A compound is a pure substance that can be broken down into two or more simpler pure substances by chemical means. Water is a compound. By means of an electric current, water can be broken down into the gases hydrogen and oxygen, both of which are elements. The ultimate breakdown products for any compound are elements. A compound's properties are always different from those of its component elements, because the elements are chemically rather than physically combined in the compound.

Each element has a unique name that, in most cases, was selected by its discoverer. Abbreviations called chemical symbols also exist for the names of the elements. ***A chemical symbol*** is a one- or two- letter designation for an element derived from the element's name. These chemical symbols are used more frequently than the elements' names.

Note that the first letter of a chemical symbol is always capitalized and the second is not. Two-letter chemical symbols are often, but not always, the first two letters of the element's name.

As soon as chemists realized that mass – not volume, density or some other measurable property – was the fundamental property that was conserved during chemical reactions, they began to try to establish a correct scale of atomic masses (atomic weights) for all the elements. The result of their years of work is the table of natural atomic weights. The molecular weights of molecular compounds and the formula weights of nonmolecular compounds (such as salts) are found by adding the atomic weights of all the constituent atoms.

Central to all chemical calculations is the concept of the mole. A mole of any substance is the quantity that contains as many particles of the substance as there are atoms in exactly 12 g of carbon – 12. Thus a mole of a substance is a quantity in grams that is numerically equal to its molecular weight expressed in atomic mass units. The number of particles in a mole is called Avogadro's number:

$$N = 6.022 \cdot 10^{23} \text{ particles} \cdot \text{mole}^{-1}$$

If we know that two molecules of hydrogen gas, H_2, react with one molecule of oxygen gas, O_2, to produce two molecules of water, H_2O, then we can predict that 2 moles of H_2, or 4.032 g, will react with 1 mole of O_2, or 31.999 g, to yield 2 moles of water, or 36.031 g. The check addition, $4.032 + 31.999 = 36.031$, verifies the conservation of mass during the reaction. The chemist measures substances in grams, by weighing them. Yet it is more meaningful to convert these quantities from grams to moles, because then one is working with relative molecular proportions, scaled up by a uniform factor of N.

1.4 Fundamental chemical laws

The law of conservation of mass (Lavoisier, 18th century): Lavoisier was one of the first to carry out quantitatively accurate chemical measurements. He demonstrated that combustion required oxygen, and he demonstrated oxygen's role in the rusting of metals. His observations led him to deduce the following general law known as the law of conservation of mass: “In every chemical transformation, an equal quantity of matter exists before and after the reaction”.

The law of definite proportions (Joseph Proust, shortly after Lavoisier). Proust studied metal compounds, including metal oxides, carbonates and sulfides. From the work of Robert Boyle in the 17th century, it was understood that substances that could be broken down into more fundamental components were mixtures or compounds. Substances that could not be further broken down were referred to as elements. Thus, Proust deduced the so-called law of definite proportions: “In a given chemical compound, the proportions by mass of the elements that compose it are fixed, independent of the origin of the compound or its mode of preparation”. This is basically saying that sodium chloride, for example, is always NaCl, no matter how it is obtained, made, or prepared. There are no “intermediate” compounds.

The law of multiple proportions: (John Dalton, shortly after Proust). Studied gases and gaseous mixtures under different external conditions. Building on Proust's work, he noted that mathematically discrete manner in which elements combined to form different compounds. For example, in carbon monoxide (CO), the mass ratio of oxygen to carbon and in carbon dioxide (CO). Thus, since the amount of carbon is fixed in each compound, we can look at how the amount of oxygen varies, and we find that. The generalization of this idea is the law of multiple proportions: “When two elements form a series of compounds, the masses of one that combine with a fixed mass of the other are in the ratio of (small) integers to each other”. This law is obeyed by all gaseous compounds, which is what Dalton studied. Certain solids are exceptions to both this rule and the law of definite proportions. An example is the solid wustite, which can range its composition, depending on the mode of preparation.

The law of combining volumes (Joseph Gay-Lussac, Amedeo Avagadro, Stanislao Cannizzaro, early 19th century following Dalton). Again, based on studies of gases and how they combine, the law of combining volumes has been attributed to these three. The generalization of the observations is stated as follows: “When two gases are allowed to react, such that the gases are at the same temperature and pressure, the volumes of each gas consumed will be in the ratio of small integers. Moreover, the ratio of the volume of each product gas to the volume of either reacting gas will be a ratio of simple integers”.

1.5 Chemical reactions and equations

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. Chemical reactions can be either spontaneous, requiring no input of energy, or non-spontaneous, typically following the input of some type of energy, viz heat, light or electricity. Classically, chemical reactions encompass changes that strictly involve the motion of electrons in the forming and breaking of chemical bonds, although the general concept of a chemical reaction, in particular the notion of a chemical equation, is applicable to transformations of elementary particles, as well as nuclear reactions.

The substance (or substances) initially involved in a chemical reaction are called reactants or reagents. Chemical reactions are usually characterized by a chemical change, and they yield one or more products, which usually have properties different from the reactants. Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with chemical equations, which graphically present the starting materials, end products, and sometimes intermediate products and reaction conditions.

Chemical equations are used to graphically illustrate chemical reactions. They consist of chemical or structural formulas of the reactants on the left and those of the products on the right. They are separated by an arrow (→) which indicates the direction and type of the reaction. The tip of the arrow points in the direction in which the reaction proceeds.

For example, when propane gas, C_3H_8, is burned in oxygen, the products are carbon dioxide and water. This statement can be written as a chemical equation:

$$C_3H_8 + O_2 \rightarrow CO_2 + H_2O \qquad (1.1)$$

If chemistry were not a quantitative science, then this description of the reaction, identifying both the reactants and the products, would be adequate. But we expect more from a chemical equation. How many molecules of oxygen are required per molecule of propane, and how many molecules of carbon dioxide and water result? Equation 1.1 is an unbalanced equation. When we add numerical coefficients (placed to the left of the formula) that tell how many of each kind of molecule are involved, then there will be the same number of each kind of atom on the left and right sides of the equation, since atoms are neither created nor destroyed in a chemical reaction. The result will be a balanced equation.

To balance equation 1.1, we note first that the 3 carbon atoms on the left will lead to 3 molecules of CO_2 as products, each requiring 2 oxygen atoms, or 6 oxygens in all. Similarly, the 8 hydrogen atoms in propane will produce 4 molecules of water, requiring 4 more oxygen atoms. This total of 10 oxygens on the right must come from 5 molecules of O_2. The correct coefficients for the four substances in equation 1.2 are therefore 1, 5, 3, and 4.

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (1.2)$$

Each side of this balanced equation 1.2 contains 3 carbon atoms, 8 hydrogen atoms, and 10 oxygen atoms.

CONCEPTS TO REMEMBER

Chemistry. Chemistry is the field of study that is concerned with the characteristics, composition, and transformations of matter. Matter. Matter, the substances of the physical universe, is anything that has mass and occupies space. Matter exists in three physical states: solid, liquid, and gas.

Properties of matter. Properties, the distinguishing characteristics of a substance that are used in its identification and description, are of two types: physical and chemical. Physical properties are properties that can be observed without changing a substance into another substance. Chemical properties are properties that matter exhibits as it undergoes or resists changes in chemical composition. The failure of a substance to undergo change in the presence of another substance is considered a chemical property.

Changes in matter. Changes that can occur in matter are classified into two types: physical and chemical. A physical change is a process that does not alter the basic nature (chemical composition) of the substance under consideration. No new substances are ever formed as a result of a physical change. A chemical change is a process that involves a change in the basic nature (chemical composition) of the substance. Such changes always involve conversion of the material or materials under consideration into one or more new substances that have properties and composition distinctly different from those of the original materials.

Pure substances and mixtures. All specimens of matter are either pure substances or mixtures. A pure substance is a form of matter that has a definite and constant composition. A mixture is a physical combination of two or more pure substances in which the pure substances retain their identity.

Types of mixtures. Mixtures can be classified as heterogeneous or homogeneous on the basis of the visual recognition of the components present. A heterogeneous mixture contains visibly different parts or phases each of which has different properties. A homogeneous mixture contains only one phase, which has uniform properties throughout.

Types of pure substances. A pure substance can be classified as either an element or a compound on the basis of whether it can be broken down into two or more simpler substances by chemical means. Elements cannot be broken down into simpler substances. Compounds yield two or more simpler substances when broken down. There are 117 pure substances that qualify as elements. There are millions of compounds.

Chemical symbols. Chemical symbols are a shorthand notation for the names of the elements. Most consist of two letters; a few involve a single letter. The first letter of a chemical symbol is always capitalized, and the second letter is always lowercase.

Atoms and molecules. An atom is the smallest particle of an element that can exist and still have the properties of the element. Free isolated atoms are rarely encountered in nature. Instead, atoms are almost always found together in aggregates or clusters. A molecule is a group of two or more atoms that functions as a unit because the atoms are tightly bound together.

Types of molecules. Molecules are of two types: homoatomic and heteroatomic. Homoatomic molecules are molecules in which all atoms present are of the same kind. A pure substance containing homoatomic molecules is an element. Heteroatomic molecules are molecules in which two or more different kinds of atoms are present. Pure substances that contain heteroatomic molecules must be compounds.

Chemical formulas. Chemical formulas are used to specify compound composition in a concise manner. They consist of the symbols of the elements present in the compound and numerical subscripts (located to the right of each symbol) that indicate the number of atoms of each element present in a molecule of the compound.

SAMPLE PROBLEMS WITH SOLUTIONS

Problem 1

Classify each of the following properties for selected metals as a physical property or a chemical property.

A. Iron metal rusts in an atmosphere of moist air.
B. Mercury metal is a liquid at room temperature.
C. Nickel metal dissolves in acid to produce a light green solution.
D. Potassium metal has a melting point of 63°C.

Solution

A. Chemical property. The interaction of iron metal with moist air produces a new substance (rust).
B. Physical property. Visually determining the physical state of a substance does not produce a new substance.
C. Chemical property. A change in color indicates the formation of a new substance.
D. Physical property. Measuring the melting point of a substance does not change the substance's composition.

Problem 2

Classify each of the following statements about changes in matter as physical or chemical.

A. The fashioning of a piece of wood into a round table leg
B. The vigorous reaction of potassium metal with water to produce hydrogen gas
C. Straightening a bent piece of iron with a hammer
D. The ignition and burning of a match

Solution

A. Physical. The table leg is still wood. No new substances have been formed.

B. Chemical. A new substance, hydrogen, is produced.
C. Physical. The piece of iron is still a piece of iron.
D. Chemical. New gaseous substances, as well as heat and light, are produced as the match burns.

Problem 3

For each of the following chemical formulas, determine how many atoms of each element are present in one molecule of the compound.

A. HCN – hydrogen cyanide, a poisonous gas.
B. $C_{18}H_{21}NO_3$ – codeine, a pain-killing drug.
C. $Ca_{10}(PO_4)_6(OH)_2$ – hydroxyapatite, present in tooth enamel.

Solution

A. One atom each of the elements hydrogen, carbon, and nitrogen is present. Remember that the subscript 1 is implied when no subscript is written.
B. This formula indicates that 18 carbon atoms, 21 hydrogen atoms, 1 nitrogen atom, and 3 oxygen atoms are present in one molecule of the compound.
C. There are 10 calcium atoms. The amounts of phosphorus, hydrogen, and oxygen are affected by the subscripts outside the parentheses. There are 6 phosphorus atoms and 2 hydrogen atoms present. Oxygen atoms are present in two locations in the formula. There are a total of 26 oxygen atoms: 24 from the PO_4 subunits ($6 \cdot 4$) and 2 from the OH subunits ($2 \cdot 1$).

INDIVIDUAL TEST PAPER

Exercise 1

Classify each of the following properties for selected metals as a *physical* property or a *chemical* property.

A. Titanium metal can be drawn into thin wires.
B. Silver metal shows no sign of reaction when placed in hydrochloric acid.
C. Copper metal possesses a reddish brown color.
D. Beryllium metal, when inhaled in a finely divided form, can produce serious lung disease.

Exercise 2

Complete each of the following statements about changes in matter by placing the word *physical* or *chemical* in the blank.

A. The destruction of a newspaper through burning involves a ______ change.
B. The grating of a piece of cheese is a _______ change.
C. The heating of a blue powdered material to produce a white glassy substance and a gas is a ______ change.
D. The crushing of ice cubes to make ice chips is a ______ change.

Exercise 3

For each of the following chemical formulas, determine how many atoms of each element are present in one molecule of the compound.

A. H_2SO_4 – sulfuric acid, an industrial acid
B. $C_{17}H_{20}N_4O_6$ – riboflavin, a B vitamin
C. $Ca(NO_3)_2$ – calcium nitrate, used in fireworks to give a reddish color

Exercise 4

Trinitrotoluene (TNT), $C_7H_5N_3O_6$, combines violently with oxygen to produce CO_2, water, and N_2. Write a balanced chemical equation for the explosion.

CHAPTER 2 Atomic structure and the periodic table

2.1 Constituents of the atom

The atom of any element consists of three basic types of particles the electron (a negatively charged particle), the proton (a positively charged particle), and the neutron (a neutrally charged particle). The protons and neutrons occupy the nucleus while the electrons are outside of the nucleus. The protons and neutrons contribute very little to the total volume but account for the majority of the atom's mass. However, the atoms volume is determined the elections, which contribute very little to the mass.

The atomic number (Z) of an element is the number of protons within the nucleus of an atom of that element. In a neutral atom, the number of protons and electrons are equal and the atomic number also indicates the number of electrons.

The mass number (A) is the sum of the protons and neutrons present in the atom, The number of neutrons can be determined by (A – Z). The symbol for denoting the atomic number and mass number for an element X is as follows:

$$^{A}_{Z}X$$

Atoms that have the same atomic number (equal number of protons) but different atomic masses (unequal number of neutrons) are referred to as isotopes. For example, carbon consists of two isotopes, carbon – **12** and carbon – 13:

$$^{12}_{6}\text{C} \qquad\qquad\qquad ^{13}_{6}\text{C}$$

The atomic mass unit (amu) is defined as 1/12 the mass of a carbon-12 isotope. The relative ***atomic mass*** of an element is the weighted average of the isotopes relative to 1/12 of the carbon –12 isotope. For example, the atomic mass of neon is 20.17 amu and is calculated from the following data: neon – 19 (amu of 19.99245, natural abundance of 90.92 %), neon – 20 (amu of 20.99396, natural abundance of 0.260 %) and neon – 2l (amu of 21.99139, natural abundance of 8.82 %):

$$\text{a.m. neon} – (19.99245·0.9092) + (20.99396·0.00260) +$$

$$+ (21.99139 · 0.0882) = 20.17 \text{ amu}$$

The relative molecular mass is the sum of the atomic masses for each atom in the molecule. For $H_2SO_4 = (1·2)+32+(16·4) = 98$.

The mole (mol) is simply a unit of quantity, it represents a certain amount of material, i.e. atoms or molecules. The numerical value of one mole is $\mathbf{6.023·10^{23}}$ and is referred to as ***Avogadro's number***. The mole is defined as the mass, in grams, equal to the atomic mass of an element or molecule. Therefore, **1** mole of carbon weighs **12** grams and contains $\mathbf{6.023·10^{23}}$ carbon atoms. The following formula can be used to find the number of moles:

$$\text{mole} = \frac{\text{mass in grams}}{\text{molecular mass}} \qquad (2.1)$$

2.2 Quantum number

From quantum mechanics a set of equations called wave equations are obtained. A series of solutions to these equations, called wave functions, gives the four quantum numbers required to describe the placement of the electrons in the hydrogen atom or in other atoms (table 2.1).

Table 2.1 – Quantum numbers and electron distribution

Shell	Principal quantum number $\boldsymbol{n_s}$	Angular momentum quantum number λ	Orbital designation	Magnetic quantum number $\boldsymbol{m_\lambda}$	Spin quantum number $\boldsymbol{m_s}$	Total number of electrons per orbital
K	1	0	s	0	– ½, + ½	2
L	2	0	s	0	– ½, + ½	2
		1	p_x	–1	– ½, + ½	6
			p_y	0	– ½, + ½	
			p_z	+1	– ½, + ½	
M	3	0	s	0	– ½, + ½	2
		1	p_x	−1	– ½, + ½	6
			p_y	0	– ½, + ½	
			p_z	+1	– ½, + ½	
		2	d_{xy}	−2	– ½, + ½	10
			d_{xz}	−1	– ½, + ½	
			d_{yz}	0	– ½, + ½	
			d_{z2}	+1	– ½, + ½	
			d_{x2-y2}	+2	– ½, + ½	

The principal quantum number ($\boldsymbol{n_s}$) determines the energy of an orbital and has a value of n = 1, 2, 3, 4, ... The angular momentum quantum number (λ) determines the “shape” of the orbital and has a value of 0 to ($n - 1$) for every value of n. The magnetic quantum number (m_λ) determines the orientation of the orbital in space and has a value of $-\lambda$ to $+\lambda$. The electron spin quantum number (m_S) determines the magnetic field generated by the electron and has a value of – ½ or + ½.

The following is a summary in which the quantum numbers are used to fill the atomic orbitals:

1. No two electrons can have the same four quantum numbers. This is the Pauli exclusion principle.
2. Orbitals are filled in the order of increasing energy.
3. Each orbital can only be occupied by a maximum of two electrons and must have different spin quantum numbers (opposite spins).
4. The most stable arrangement of electrons in orbitals is the one that has the greatest number of equal spin quantum numbers (parallel spins). This is Hund’s rule.

Also note that the energy of an electron also depends on the angular momentum quantum number as well as the principal quantum number. Therefore the order that the orbitals get filled does not strictly follow the principal quantum number. The order in which orbitals are filled is given in figure 2.1.

2.3. Atomic orbitals

The quantum numbers mentioned earlier were obtained as solutions to a set of wave equations. These wave equations cannot tell precisely where an electron is at any given moment or how fast it is moving, but rather it states the probability of finding the electron at a particular place. An orbital is a region of space where the electron is most likely to be found. An orbital has no definite boundary to it, but can be thought of as a cloud with a specific shape. Also, the orbital is not uniform throughout, but rather densest in the region where the probability of finding the electron is highest.

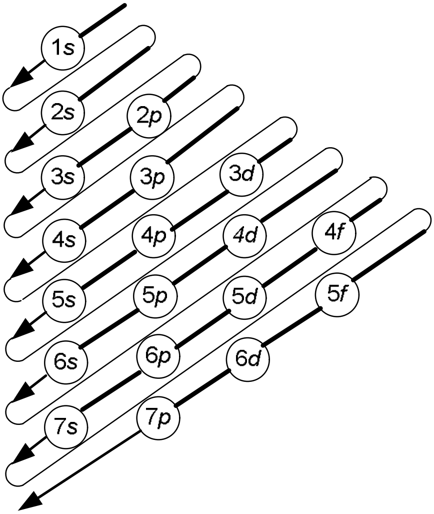
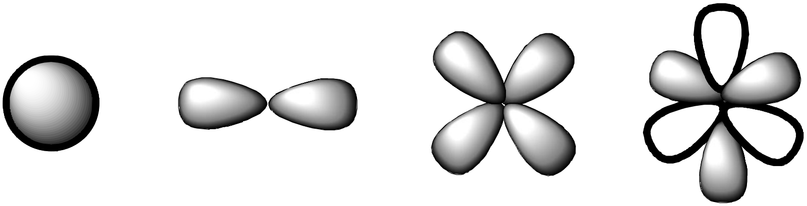


Fig. 2.1 – The order for filling electron subshells with electrons follows the order given by the arrows in this diagram. Start with the arrow at the top of the diagram and work toward the bottom of the diagram, moving from the bottom of one arrow to the top of the next-lower arrow

The shape of an orbital represents 90 % of the probability of finding the electron within that space. As the quantum numbers change so do the shapes and direction of the orbitals. Figure 2.2 show the shapes for principal quantum number n – 1,2, and 3.



s – orbital *p* – orbital *d* – orbital *f* – orbital

Fig. 2.2 – Graphic type of orbitals

2.4 Ionization energy

Ionization energy (I.E.) is the minimum amount of energy needed to remove an electron from a gasous atom or ion, and is expressed in electron volts (eV).

Going across the periodic table the I.E. increases due to the fact that the principal energy level (principal quantum number) remains the same while the number of electrons increase, thereby enhancing the electrostatic attraction between the protons in the nulceus and the electrons. Going down the table the I.E. decreases because the outer electrons are now further from the nucleus and the protons.

2.5 Electronegativity

Electronegalivity (X) is the relative attraction of an atom for an electron in a covalent bond. But due to the complexity of a covalent bond it is not possible to define precise electronegativity values. Originally the element fluorine, whose atoms have the greatest attraction for an election, was given an arbitraiy value of

4.0. All other electronegativity values are based on this.

Note that the greater the difference in electronegativities the more ionic in nature is the bond, and the smaller the difference the more covalent is the bond.

Going across the periodic table the electronegativity increases because the principal energy level remain the same and the electrostatic attraction increases. The atoms also have a desire to have the most stable configuration which is that of the noble gas configuration. Going down the table the electronegativity decreases due to the increased distance from the nucleus.

The radius of an atom can be estimated by taking half the distance between the nucleus of two of the same atoms. For example, the distance between the nuclei of I_2 is 2.66 Å**,** half that distance would be the radius of atomic iodine or 1.33 Å. Using this method the atomic radius of nearly all the elements can be estimated.

Note that going across the periodic table, the atomic radius decreases. This is due to the fact that the principal energy level (principal quantum number) remains the same, but the number of electrons increase. The increase in the number of electrons causes an increase in the electrostatic attraction which causes the radius to decrease. However, going down the periodic table the principal energy level increases and hence the atomic radius increases.

CONCEPTS TO REMEMBER

Subatomic particles. Subatomic particles, the very small building blocks from which atoms are made, are of three major types: electrons, protons, and neutrons. Electrons are negatively charged, protons are positively charged, and neutrons have no charge. All neutrons and protons are found at the center of the atom in the nucleus. The electrons occupy the region about the nucleus. Protons and neutrons have much larger masses than electrons.

Atomic number and mass number. Each atom has a characteristic atomic number and mass number. The atomic number is equal to the number of protons in the nucleus of the atom. The mass number is equal to the total number of protons and neutrons in the nucleus.

Isotopes. Isotopes are atoms that have the same number of protons and electrons but have different numbers of neutrons. The isotopes of an element always have the same atomic number and different mass numbers. Isotopes of an element have the same chemical properties.

Atomic mass. The atomic mass of an element is a calculated average mass. It depends on the percentage abundances and masses of the naturally occurring isotopes of the element.

Periodic law and periodic table. The periodic law states that when elements are arranged in order of increasing atomic number, elements with similar chemical properties occur at periodic (regularly recurring) intervals. The periodic table is a graphical representation of the behavior described by the periodic law. In a modern periodic table, vertical columns contain elements with similar chemical properties. A group in the periodic table is a vertical column of elements. A period in the periodic table is a horizontal row of elements.

Electron shell. An electron shell contains electrons that have approximately the same energy and spend most of their time approximately the same distance from the nucleus.

Electron subshell. An electron subshell contains electrons that all have the same energy. The number of subshells in a particular shell is equal to the shell number. Each subshell can hold a specific maximum number of electrons. These values are 2, 6, 10, and 14 for *s*-, *p*-, *d*-, and *f*- subshells, respectively.

Electron orbital. An electron orbital is a region of space about a nucleus where an electron with a specific energy is most likely to be found. Each subshell consists of one or more orbitals. For *s*-, *p*-, *d*-, and *f*- subshells there are 1, 3, 5, and 7 orbitals, respectively. No more than two electrons may occupy any orbital.

Electron configuration. An electron configuration is a statement of how many electrons an atom has in each of its subshells. The principle that electrons normally occupy the lowest-energy subshell available is used to write electron configurations.

Orbital diagram. An orbital diagram is a notation that shows how many electrons an atom has in each of its orbitals. Electrons occupy the orbitals of a subshell such that each orbital within the subshell acquires one electron before any orbital acquires a second electron. All electrons in such singly occupied orbitals must have the same spin.

Electron configurations and the periodic law. Chemical properties repeat themselves in a regular manner among the elements because electron configurations repeat themselves in a regular manner among the elements.

Electron configurations and the periodic table. The groups of the periodic table consist of elements with similar electron configurations. Thus the location of an element in the periodic table can be used to obtain information about its electron configuration.

Classification system for the elements. On the basis of electron configuration, elements can be classified into four categories: noble gases (far right column of the periodic table); representative elements (*s*- and *p*- areas of the periodic table, with the exception of the noble gases); transition elements (*d*- area of the periodic table); and inner transition elements (*f*- area of the periodic table).

SAMPLE PROBLEMS WITH SOLUTIONS

Problem 1

Determine the following for an atom whose complete chemical symbol is ${}^{26}_{12}\mathrm{Mg}$.

A. The total number of subatomic particles present in the atom.
B. The total number of subatomic particles present in the nucleus of the atom.
C. The total number of nucleons present in the atom.
D. The total charge (including sign) associated with the nucleus of the atom.

Solution

A. The mass number gives the combined number of protons and neutrons present. The atomic number gives the number of electrons present. Adding these two numbers together gives the total number of subatomic particles present. There are 38 subatomic particles present (26 + 12 = 38).
B. The nucleus contains all protons and all neutrons. The mass number (protons/neutrons), thus, gives the total number of subatomic particles present in the nucleus of an atom. There are 26 subatomic particles present in the nucleus.

C. A nucleon is any subatomic particle present in the nucleus. Thus, both protons and neutrons are nucleons. There are 26 such particles present in the nucleus. Parts *b* and *c* of this example are, thus, asking the same thing using different terminology.
D. The charge associated with a nucleus originates from the protons present. It will always be positive because protons are positively charged particles. The atomic number, 12, indicates that 12 protons are present. Thus, the nuclear charge is 12.

Problem 2

What is the chemical symbol of the element that fits each of the following descriptions based on periodic table location?

A. Located in both period 3 and group IV.
B. The period 4 noble gas.
C. The period 2 alkaline earth metal.
D. The period 3 halogen.

Solution

A. Period 3 is the third row of elements and group IV is the fifth column from the right side of the periodic table. The element that has this column–row (period–group) location is Si (silicon).
B. The noble gases are the elements of group VIII (the right-most column in the periodic table). The period 4 (fourth row) noble gas is Kr (krypton).
C. The alkaline earth metals are the elements of group II (the second column from the left side of the periodic table). The

period 2 (second row) alkaline earth metals is Be (beryllium).

D. The halogens are the elements of group VII (the second column from the right side of the periodic table). The period 3 (third row) halogen is Cl (chlorine).

Problem 2

Write the electron configurations for the Strontium (atomic number 38).

Solution

The number of electrons in a strontium atom is 38. Remember that the atomic number gives the number of electrons. We will need to fill subshells, in order of increasing energy, until 38 electrons have been accommodated. The 1*s*, 2*s*, and 2*p* subshells fill first, accommodating a total of 10 electrons among them.

$$1s^2 2s^2 2p^6 3s^2 3p^6 \ldots$$

We have accommodated 18 electrons at this point. We still need to add 20 more electrons to get our desired number of 38. The 4*s* subshell fills next, followed by the 3*d* subshell, giving us 30 electrons at this point.

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} \ldots$$

Note that the maximum electron population for *d* subshells is 10 electrons. Eight more electrons are needed, which are added to the next two higher subshells, the 4*p* and the 5*s*. The 4*p* subshell can accommodate 6 electrons, and the 5*s* can accommodate 2 electrons.

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 \ldots$$

To double-check that we have the correct number of electrons, 38, we add the superscripts in our final electron configuration.

$$2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 = 38$$

The sum of the superscripts in any electron configuration should add up to the atomic number if the configuration is for a neutral atom.

INDIVIDUAL TEST PAPER

Exercise 1

Design electronic and electronic-graphic formulas of the elements given in the table 2.2.

Indicate the family of each element (*s*-, *p*-, *d*-, *f*-) and an amount of valence electrons both in ground and excited states of atom.

Exercise 2

Which of electronic configurations given in the table 2.3 is impossible? What is the reason of its impossibility in the ground state of atom?

Exercise 3

Indicate the period, group and subgroup of the elements if it is known the electronic structure of outermost levels as given in the table 2.4. What are the names and numbers of these elements?

Table 2.2 – Variants of the problem

Variant	Elements	Variant	Elements
1	Ca, O, Ta	13	Ti, Fe, Pm
2	Pr, Na, S	14	In, F, Zr
3	Se, Ni, Nd	15	Tl, Cl, Nb
4	Li, Cu, Tl	16	Na, Br, Ru
5	Mg, Po, Zr	17	Fe, At, Be
6	N, Fr, Eu	18	Ba, Zn, Pb
7	Be, P, Cd	19	C, Os, Mg
8	As, Au, Mg	20	Cd, Sb, Rh
9	Rb, Hg, Te	21	Si, Co, Sr
10	Sr, Sc, Br	22	Pd, Cs Cf
11	Al, Sn, Mn	23	K, Ti, Ge
12	Tl, Pb, Th	24	Hf, Ra, Sb

Table 2.3 – Variants of the problem

Variant	Electronic configuration	Variant	Electronic configuration	Variant	Electronic configuration
1	$1p^3$; $3d^3$	9	$2d^3$; $4p^2$	17	$1p^6$; $4d^4$
2	$4s^1$; $4p^7$	10	$3f^3$; $2p^5$	18	$3p^5$; $1d^3$
3	$3d^1$; $2d^4$	11	$2p^2$; $3d^{13}$	19	$2d^5$; $3s1^2$
4	$3p^8$; $3d^4$	12	$2p^{14}$; $3d^{10}$	20	$5p^8$; $6s^1$
5	$3d^{12}$; $5p^6$	13	$1d^2$; $4\ p^5$	21	$4s^4$; $3d^8$
6	$4p^3$; $2f^1$	14	$4p^2$; $3f^{10}$	22	$3p^5$; $3f^8$
7	$4s^3$; $5d^8$	15	$4d^{14}$; $4\ f^5$	23	$3d^{10}$; $4p^8$
8	$4f^{11}$; $3p^8$	16	$2p^6$; $2d^4$	24	$3d^{11}$; $4f^{12}$

Table 2.4 – Variants of the problem

Variant	The electronic structure of outermost levels	Variant	The electronic structure of outermost levels
1	$2p^{6}3s^{2}$; $4s^{2}4p^{5}$	13	$3s^{2}3p^{5}$; $1s^{2}2s^{1}$
2	$3d^{10}4s^{2}$; $6s^{2}6p^{1}$	14	$6s^{2}6p^{3}$; $4d^{6}5s^{2}$
3	$3d^{6}4s^{2}$; $5p^{6}6s^{1}$	15	$2p^{6}3s^{2}$; $3d^{6}4s^{2}$
4	$3s^{2}3p^{2}$; $2p^{6}3s^{1}$	16	$4p^{6}5s^{1}$; $5d^{1}6s^{2}$
5	$4d^{5}5s^{2}$; $4s^{2}4p^{6}$	17	$6d^{2}7s^{2}$; $4d^{8}5s^{2}$
6	$5d^{2}6s^{2}$; $3p^{6}4s^{2}$	18	$5d^{3}6s^{2}$; $6p^{6}7s^{2}$
7	$5p^{6}6s^{2}$; $6s^{2}6p^{2}$	19	$4s^{2}4p^{4}$; $3d^{7}4s^{2}$
8	$5d^{4}6s^{2}$; $4d^{10}5s^{2}$	20	$3d^{8}4s^{2}$; $5s^{2}5p^{3}$
9	$6s^{2}6p^{5}$; $2s^{2}2p^{4}$	21	$5p^{6}6s^{1}$; $5d^{5}6s^{2}$
10	$3p^{6}4s^{1}$; $5d^{5}6s^{2}$	22	$5s^{2}5p^{2}$; $6p^{6}7s^{2}$
11	$5s^{2}5p^{5}$; $5d^{7}6s^{2}$	23	$3s^{2}3p^{3}$; $5s^{2}5p^{6}$
12	$4p^{6}5s^{2}$; $3d^{4}4s^{2}$	24	$6d^{8}7s^{2}$; $1s^{2}2s^{2}$

Exercise 4

Design the electronic formula of element which has an oxidation number given in the table 2.5.

Table 2.5 – Variants of the problem

Variant	Elements and their oxidation numbers	Variant	Elements and their oxidation numbers
1	Mg(+2); I(−1);Ni(+3)	6	Ru(+6); Rb(+1); N(−3)
2	Ni(+2); Na(+1); O(−2)	7	Ru(+8); Ba(+2); Cl(−1)
3	Fe(+2); Ca(+2); N(−3)	8	Be(+2); P(–3); Ta(+5)
4	Mn(+2); Fe(+3); Br(−1)	9	P(+3); Se(+6); F(−1)
5	Co(+3); S(−2); S(+6)	10	O(−2); Cl(+7); Fe(+6)

Continued of table 2.5

Variant	Elements and their oxidation numbers	Variant	Elements and their oxidation numbers
11	Ru(+2); Al(+3); S(−2)	18	Ge(−4); Mn(+6); W(+2)
12	Cs(+1); Sb(–3); C(+4)	19	W(+6); As(+5); C(−4)
13	Sc(+3); N(+3); Te(−2)	20	Cr(+3); Mo(+2); S(−2)
14	V(+2); Rh(+6);Hg(+2)	21	Sn(+2); Cs(+1); Br(−1)
15	Pb(+2); Sn(+2); As(−3)	22	In(+3); Bi(+3); Te(−2)
16	Sn(+4); Bi(+5); N(−3)	23	As(+5); Mo(+2); H(1)
17	Mn(+2); Nb(+5); I(–1)	24	Hg(+2); Pb(+4); S(−2)

CHAPTER 3

Chemical bonding: the covalent and the ionic bond models

3.1 Chemical bond

Chemical compounds are conveniently divided into two broad classes called ***ionic compounds*** and ***molecular compounds***. Ionic and molecular compounds can be distinguished from each other on the basis of general physical properties. Ionic compounds tend to have high melting points (500 – 2000 °C) and are good conductors of electricity when they are in a molten (liquid) state or in solution. Molecular compounds, on the other hand, generally have much lower melting points and tend to be gases, liquids, or low- melting point solids. They do not conduct electricity in the molten state. Ionic compounds, unlike molecular compounds, do not have molecules as their basic structural unit. Instead, an extended array of positively and negatively charged particles called ***ions*** is present.

Some combinations of elements produce ionic compounds, whereas other combinations of elements form molecular compounds. ***A chemical bond*** is the attractive force that holds two atoms together in a more complex unit. Chemical bonds form as a result of interactions between electrons found in the combining atoms. Thus, the nature of chemical bonds is closely linked to electron configurations.

Corresponding to the two broad categories of chemical compounds are two types of chemical attractive forces (chemical bonds): ionic bonds and covalent bonds. ***An ionic bond*** is a chemical bond formed through the transfer of one or more electrons from one atom or group of atoms to another atom or group of atoms. As its name suggests, the ionic bond model (electron transfer) is used in describing the attractive forces in ionic compounds. ***An ionic compound*** is a compound in which ionic bonds are present.

A covalent bond is a chemical bond formed through the sharing of one or more pairs of electrons between two atoms. The covalent bond model (electron sharing) is used in describing the attractions between atoms in molecular compounds. ***A molecular compound*** is a compound in which covalent bonds are present.

Even before we consider the details of these two bond models, it is important to emphasize that the concepts of ionic and covalent bonds are actually "convenience concepts." Most bonds are not 100 % ionic or 100 % covalent. Instead, most bonds have some degree of both ionic and covalent character – that is, some degree of both the transfer and the sharing of electrons. However, it is easiest to understand these intermediate bonds (the real bonds) by relating them to the pure or ideal bond types called ionic and covalent.

Two concepts fundamental to understanding both the ionic and the covalent bonding models are:

1. Not all electrons in an atom participate in bonding. Those that do are called *valence electrons.*

2. Certain arrangements of electrons are more stable than others, as is explained by the *octet rule.*

3.2 Valence and Lewis symbols. The octet rule

Certain electrons called valence electrons are particularly important in determining the bonding characteristics of a given atom. ***A valence electron*** is an electron in the outermost electron shell of a representative element or noble-gas element. Note the restriction on the use of this definition; it applies only to representative elements and noble-gas elements. For such elements, valence electrons are always found in either *s* or *p* subshells. (We will not consider in this text the more complicated valence electron definitions for transition elements or inner transition elements; here, the presence of incompletely filled *d*- or *f*- subshells is a complicating factor.)

The number of valence electrons in an atom of a representative element can be determined from the atom's electron configuration.

Scientists have developed a shorthand system for designating the number of valence electrons present in atoms of an element. This system involves the use of Lewis symbols. ***A Lewis symbol*** is the chemical symbol of an element surrounded by dots equal in number to the number of valence electrons present in atoms of the element. Figure 4.1 gives the Lewis symbols for the first 20 elements, all of which are representative elements or noble gases. Lewis symbols, named in honor of the American chemist Gilbert N. Lewis, who first introduced them, are also frequently called ***electron-dot structures***.

The general practice in writing Lewis symbols is to place the first four "dots" separately on the four sides of the chemical symbol and then begin pairing the dots as further dots are added. It makes no difference on which side of the symbol the process of adding dots begins.

Three important generalizations about valence electrons:

1. Representative elements in the same group of the periodic table have the same number of valence electrons. This should not be surprising. Elements in the same group in the periodic table have similar chemical properties as a result of their similar outer-shell electron configurations. The electrons in the outermost shell are the valence electrons.

2. The number of valence electrons for representative elements is the same as the Roman numeral periodic-table group number. For example, the Lewis symbols for oxygen and sulfur, which are both members of group VIA, have six dots. Similarly, the Lewis symbols of hydrogen, lithium, sodium, and potassium, which are all members of group IA, have one dot.

3. The maximum number of valence electrons for any element is eight. Only the noble gases, beginning with neon, have the maximum number of eight electrons. Helium, which has only two valence electrons, is the exception in the noble- gas family. Obviously, an element with a total of two electrons cannot have eight valence electrons. Although electron shells with n greater than 2 are capable of holding more than eight electrons, they do so only when they are no longer the outermost shell and thus are not the valence shell. For example, arsenic has 18 electrons in its third shell; however, shell 4 is the valence shell for arsenic.

A key concept in elementary bonding theory is that certain arrangements of valence electrons are more stable than others. The term ***stable*** as used here refers to the idea that a system, which in this case is an arrangement of electrons, does not easily undergo spontaneous change.

The valence electron configurations of the noble gases (helium, neon, argon, krypton, xenon, and radon) are considered the ***most stable of all valence electron configurations***. All of the noble gases except helium possess eight valence electrons, which is the maximum number possible. Helium's valence electron configuration is $1s^2$. All of the other noble gases possess $\boldsymbol{ns^2np^6}$ valence electron configurations, where ***n*** has the maximum value found in the atom.

Except for helium, all the noble-gas valence electron configurations have the outermost ***s*** and ***p*** subshells ***completely filled***.

The conclusion that an ns^2np^6 configuration ($1s^2$ for helium) is the most stable of all valence electron configurations is based on the chemical properties of the noble gases. The noble gases are the ***most unreactive*** of all the elements. They are the only elemental gases found in nature in the form of individual uncombined atoms. There are no known compounds of helium and neon, and only a few compounds of argon, krypton, xenon, and radon are known. The noble gases have little or no tendency to form bonds to other atoms.

Atoms of many elements that lack the very stable noble-gas valence electron configuration tend to acquire it through chemical reactions that result in compound formation. This observation is known as the ***octet rule:*** in forming compounds, atoms of elements lose, gain, or share electrons in such a way as to produce a noble-gas electron configuration for each of the atoms involved.

3.3 The ionic bond model. Lewis structures for ionic compounds

Electron transfer between two or more atoms is central to the ionic bond model. This electron transfer process produces charged particles called ions. ***An ion*** is an atom (or group of atoms) that is electrically charged as a result of the loss or gain of electrons. An atom is neutral when the number of protons (positive charges) is equal to the number of electrons (negative charges). Loss or gain of electrons destroys this proton-electron balance and leaves a net charge on the atom.

If an atom ***gains*** one or more electrons, it becomes a ***negatively*** charged ion; excess negative charge is present because electrons outnumber protons. If an atom ***loses*** one or more electrons, it becomes a ***positively*** charged ion; more protons are present than electrons. There is excess positive charge. Note that the excess positive charge associated with a positive ion is never caused by proton gain but always by electron loss. If the number of protons remains constant and the number of electrons decreases, the result is net positive charge. The number of protons, which determines the identity of an element, never changes during ion formation.

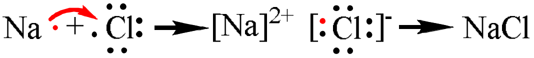
The charge on an ion depends on the number of electrons that are lost or gained. Loss of one, two, or three electrons gives ions with +1, + 2, or +3 charges, respectively. A gain of one, two, or three electrons gives ions with −1, −2, or −3 charges, respectively. (Ions that have lost or gained more than three electrons are very seldom encountered.)

The notation for charges on ions is a superscript placed to the right of the chemical symbol. Some examples of ion symbols are *positive ions*: Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+} and *negative ions*: Cl^-, Br^-, O^{2-}, S^{2-}, N^{3-}.

Note that we use a single plus or minus sign to denote a charge of 1, instead of using the notation «$^{1+}$» or «$^{1-}$». Also note that in multi charged ions, the number precedes the charge sign; that is, the notation for a charge of plus two is «$^{2+}$» rather than «$^{+2}$».

Ion formation through the loss or gain of electrons by atoms is not an isolated, singular process. In reality, electron loss and electron gain are always partner processes; if one occurs, the other also occurs. Ion formation requires the presence of two elements: a metal that can donate electrons and a nonmetal that can accept electrons. The electrons lost by the metal are the same ones gained by the nonmetal. The positive and negative ions simultaneously formed from such ***electron transfer*** attract one another. The result is the formation of an ionic compound.

Lewis structures are helpful in visualizing the formation of simple ionic compounds. ***A Lewis structure*** is a combination of Lewis symbols that represents either the transfer or the sharing of electrons in chemical bonds. ***Lewis symbols*** involve individual elements. Lewis structures involve compounds. The reaction (3.1) between the element sodium (with one valence electron) and chlorine (with seven valence electrons) is represented as follows with a Lewis structure:



(3.1)

The loss of an electron by sodium empties its valence shell. The next inner shell, which contains eight electrons (a noble-gas configuration), then becomes the valence shell. After the valence shell of chlorine gains one electron, it has the needed eight valence electrons.

3.4 The covalent bond model

We begin our discussion of covalent bonding and the molecular compounds that result from such bonding by listing several key differences between ionic and covalent bonding and the resulting ionic and molecular compounds.

1. Ionic bonds form between atoms of dissimilar elements (a metal and a nonmetal). Covalent bond formation occurs between ***similar*** or even ***identical*** atoms. Most often two nonmetals are involved.

2. Electron transfer is the mechanism by which ionic bond formation occurs. Covalent bond formation involves ***electron sharing.***

3. Ionic compounds do not contain discrete molecules. Instead, such compounds consist of an extended array of alternating positive and negative ions. In covalently bonded compounds, the basic structural unit is a molecule. Indeed, such compounds are called molecular compounds.

4. All ionic compounds are solids at room temperature. Molecular compounds may be solids (glucose), liquids (water), or gases (carbon dioxide) at room temperature.

5. An ionic solid, if soluble in water, forms an aqueous solution that conducts electricity. The electrical conductance is

related to the presence of ions (charged particles) in the solution. A molecular compound, if soluble in water, usually produces a nonconducting aqueous solution.

A covalent bond is a chemical bond resulting from two nuclei attracting the same shared electrons. Consideration of the hydrogen molecule (H_2), the simplest of all molecules, provides initial insights into the nature of the covalent bond and its formation. When two hydrogen atoms, each with a single electron, are brought together, the orbitals that contain the valence electrons ***overlap*** to create an orbital common to both atoms. The two electrons, one from each H atom, now move throughout this new orbital and are said to be ***shared*** by the two nuclei.

Once two orbitals overlap, the most favorable location for the shared electrons is the area directly between the two nuclei. Here the two electrons can simultaneously interact with (be attracted to) both nuclei, a situation that produces increased stability. This concept of increased stability can be explained by using an analogy. Consider the nuclei of the two hydrogen atoms in H_2 to be «old potbellied stoves» and the two electrons to be running around each of the stoves trying to keep warm. When the two nuclei are together (an H_2 molecule) the electrons have two sources of heat. In particular, in the region between the nuclei (the overlap region) the electrons can keep both front and back warm at the same time. This is a better situation than when each electron has only one «stove» (nucleus) as a source of heat.

A single covalent bond is a covalent bond in which two atoms share one pair of electrons. All of the bonds in all of the molecules considered in the previous section were ***single*** covalent bonds. Single covalent bonds are not adequate to explain covalent bonding in all molecules. Sometimes two atoms must share two or three pairs of electrons in order to provide a complete octet of electrons for each atom involved in the bonding. Such bonds are called ***double*** covalent bonds and ***triple*** covalent bonds.

A double covalent bond is a covalent bond in which two atoms share two pairs of electrons. A double covalent bond between two atoms is approximately twice as strong as a single covalent bond between the same two atoms; that is, it takes approximately twice as much energy to break the double bond as it does the single bond.

A triple covalent bond is a covalent bond in which two atoms share three pairs of electrons. A triple covalent bond is approximately three times as strong as a single covalent bond between the same two atoms.

The term ***multiple covalent bond*** is a designation that applies to both double and triple covalent bonds.

One of the simplest molecules possessing a multiple covalent bond is the N_2 molecule, which has a triple covalent bond. A nitrogen atom has five valence electrons and needs three additional electrons to complete its octet. In order to acquire a noble-gas electron configuration, each nitrogen atom must share three of its electrons with the other nitrogen atom. Note that all three shared electron pairs are placed in the area between the two nitrogen atoms in the Lewis structure. Just as one line is used to denote a single covalent bond, three lines are used to denote a triple covalent bond.

3.5 Valence electrons and number of covalent bonds formed. Algorithm for drawing Lewis structures

Not all elements can form double or triple covalent bonds. There must be at least two vacancies in an atom's valence electron shell prior to bond formation if it is to participate in a double bond, and at least three vacancies are necessary for the triple-bond formation. This requirement eliminates group VII. A elements (fluorine, chlorine, bromine, iodine) and hydrogen from participating in such bonds. The group VII. A elements have seven valence electrons and one vacancy, and hydrogen has one valence electron and one vacancy. All covalent bonds formed by these elements are single covalent bonds.

Double bonding becomes possible for elements that need two electrons to complete their octet, and triple bonding becomes possible when three or more electrons are needed to complete an octet. Note that the word possible was used twice in the previous sentence. Multiple bonding does not have to occur when an element has two, three, or four vacancies in its octet; single covalent bonds can be formed instead. When more than one behavior is possible, the "bonding behavior" of an element is determined by the element or elements to which it is bonded.

In the covalent bonds we have considered so far (single, double, and triple), the two participating atoms in the bond contributed the same number of electrons to the bond. There is another, ***less common*** way in which a covalent bond can form. It is possible for one atom to supply two electrons and the other atom none to a shared electron pair. ***A coordinate covalent bond*** is a covalent bond in which both electrons of a shared pair come from one of the two atoms involved in the bond. Coordinate covalent bonding enables an atom that has two or more vacancies in its valence shell to share a pair of nonbonding electrons that are located on another atom.

Drawing Lewis structures for diatomic molecules is usually straightforward and uncomplicated. However, with triatomic and even larger molecules, students often have trouble. Here is a stepwise procedure for distributing valence electrons as bonding and nonbonding pairs within a Lewis structure.

Let us apply this stepwise procedure to the molecule SO_2, a molecule in which two oxygen atoms are bonded to a central sulfur atom.

Step 1. *Calculate the total number of valence electrons available in the molecule by adding together the valence electron counts for all atoms in the molecule.*

The periodic table is a useful guide for determining this number. An SO_2 molecule has 18 valence electrons available for bonding. Sulfur (group VI) has 6 valence electrons, and each oxygen (also group VI) has 6 valence electrons. The total number is therefore 6 + 2(6) = 18.

Step 2. *Write the chemical symbols of the atoms in the molecule in the order in which they are bonded to one another, and then place a single covalent bond, involving two electrons, between each pair of bonded atoms.*

For SO_2, the S atom is the central atom. Thus we have

$$O:S:O$$

Determining which atom is the ***central atom*** – that is, which atom has the most other atoms bonded to it – is the key to determining the arrangement of atoms in a molecule or polyatomic ion. Most other atoms present will be bonded to the central atom. For common binary molecular compounds, the molecular formula can help us determine the identity of the central atom. The central atom is the atom that appears only once in the formula; for example, S is the central atom in SO_3, O is the central atom in H_2O, and P is the central atom in PF_3. In molecular compounds containing hydrogen, oxygen, and an additional element, that additional element is the central atom; for example, N is the central atom in HNO_3, and S is the central atom in H_2SO_4. In compounds of this type, the oxygen atoms are bonded to the central atom, and the hydrogen atoms are bonded to the oxygens. Carbon is the central atom in nearly all carbon-containing compounds. Neither hydrogen nor fluorine is ever the central atom.

Step 3. *Add nonbonding electron pairs to the structure such that each atom bonded to the central atom has an octet of electrons. Remember that for hydrogen, an "octet" is only 2 electrons.*

For SO_2, addition of the nonbonding electrons gives

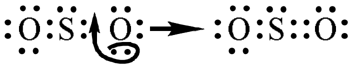
At this point, 16 of the 18 available electrons have been used.

Step 4. *Place any remaining electrons on the central atom of the structure.*

Placing the two remaining electrons on the S atom gives

Step 5. *If there are not enough electrons to give the central atom an octet, then use one or more pairs of nonbonding electrons on the atoms bonded to the central atom to form double or triple bonds.*

The S atom has only 6 electrons. Thus a nonbonding electron pair from an O atom is used to form a sulfur-oxygen double bond.



This structure now obeys the octet rule.

Step 6. *Count the total number of electrons in the completed Lewis structure to make sure it is equal to the total number of valence electrons available for bonding, as calculated in Step 1.* This step serves as a "double-check" on the correctness of the Lewis structure.

For SO_2, there are 18 valence electrons in the Lewis structure of Step 5, the same number we calculated in Step 1.

3.6 Molecular geometry

Lewis structures show the numbers and types of bonds present in molecules. They do not, however, convey any information about molecular geometry – that is, molecular shape. ***Molecular geometry*** is a description of the three-dimensional arrangement of atoms within a molecule. Indeed, Lewis structures falsely imply that all molecules have flat, two- dimensional shapes.

Molecular geometry is an important factor in determining the physical and chemical properties of a substance. Dramatic relationships between geometry and properties are often observed in research associated with the development of prescription drugs. A small change in overall molecular geometry, caused by the addition or removal of atoms, can enhance drug effectiveness and/or decrease drug side effects. Studies also show that the human senses of taste and smell depend in part on the geometries of molecules.

For molecules that contain only a few atoms, molecular geometry can be predicted by using the information present in a molecule's Lewis structure and a procedure called valence shell electron pair repulsion (VSEPR) theory. ***VSEPR theory*** is a set of procedures for predicting the molecular geometry of a molecule using the information contained in the molecule's Lewis structure.

The central concept of VSEPR theory is that electron pairs in the valence shell of an atom adopt an arrangement in space that minimizes the repulsions between the like- charged (all negative) electron pairs. The specific arrangement adopted by the electron pairs depends on the number of electron pairs present. The electron pair arrangements about a *central atom* in the cases of two, three, and four electron pairs are as follows:

1. Two electron pairs, to be as far apart as possible from one another, are found on opposite sides of a nucleus – that is, at 180° angles to one another. Such an electron pair arrangement is said to be ***linear.***

2. Three electron pairs are as far apart as possible when they are found at the corners of an equilateral triangle. In such an

arrangement, they are separated by 120° angles, giving a ***trigonal planar*** arrangement of electron pairs.

3. ***A tetrahedral*** arrangement of electron pairs minimizes repulsions among four sets of electron pairs. A tetrahedron is a four-sided solid in which all four sides are identical equilateral triangles. The angle between any two electron pairs is 109°.

3.7 Electron groups

Before we use VSEPR theory to predict molecular geometry, an expansion of the concept of an "electron pair" to that of an "electron group" is needed. This will enable us to extend VSEPR theory to molecules in which double and triple bonds are present. ***A VSEPR electron group*** is a collection of valence electrons present in a localized region about the central atom in a molecule. A VSEPR electron group may contain two electrons (a single covalent bond), four electrons (a double covalent bond) or six electrons (a triple covalent bond). VSEPR electron groups that contain four and six electrons repel other VSEPR electron groups in the same way electron pairs do. This makes sense. The four electrons in a double bond or the six electrons in a triple bond are localized in the region between two bonded atoms in a manner similar to the two electrons of a single bond.

Let us now apply VSEPR theory to molecules in which two, three, and four VSEPR electron groups are present about a central atom. Our operational rules will be:

1. Draw a Lewis structure for the molecule and identify the specific atom for which geometrical information is desired. (This atom will usually be the central atom in the molecule.);

2. Determine the number of VSEPR electron groups present about the central atom. The following conventions govern this determination:

- No distinction is made between bonding and nonbonding electron groups. Both are counted.
- Single, double, and triple bonds are all counted equally as "one electron group" because each takes up only one region of space about a central atom.

Predict the VSEPR electron group arrangement about the atom by assuming that the electron groups orient themselves in a manner that minimizes repulsions.

3.7.1 Molecules with two VSEPR electron groups

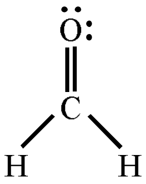
All molecules with two VSEPR electron groups are ***linear***. Two common molecules with two VSEPR electron groups are carbon dioxide (CO_2) and hydrogen cyanide (HCN), whose Lewis structures are:

$$:\ddot{O}=C=\ddot{O}: \qquad H-C\equiv N:$$

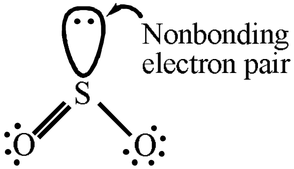
In CO_2, the central carbon atom's two VSEPR electron groups are the two double bonds. In HCN, the central carbon atom's two VSEPR electron groups are a single bond and a triple bond. In both molecules, the VSEPR electron groups arrange themselves on opposite sides of the carbon atom, which produces a linear molecule.

3.7.2 Molecules with three VSEPR electron groups

Molecules with three VSEPR electron groups have two possible molecular structures: ***trigonal planar and angular***. The former occurs when all three VSEPR electron groups are bonding and the latter when one of the three VSEPR electron groups is nonbonding. The molecules H_2CO (formaldehyde) and SO_2 (sulfur dioxide) illustrate these two possibilities. Their Lewis structures are:



Trigonal planar



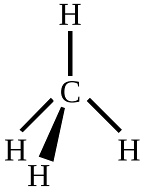
Angular

In both molecules, the VSEPR electron groups are found at the corners of an equilateral triangle.

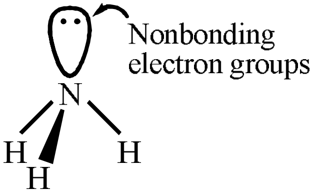
The shape of the SO_2 molecule is described as ***angular*** rather than ***trigonal planar***, because molecular geometry describes only ***atom positions***. The positions of nonbonding electron groups are not taken into account in describing molecular geometry. Do not interpret this to mean that nonbonding electron groups are unimportant in molecular geometry determinations; indeed, in the case of SO_2, it is the presence of the nonbonding electron group that makes the molecule angular rather than linear.

3.7.3 Molecules with four VSEPR electron groups

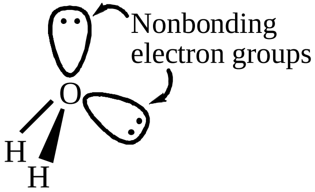
Molecules with four VSEPR electron groups have three possible molecular geometries: ***tetrahedral*** (no nonbonding electron groups present), ***trigonal pyramidal*** (one nonbonding electron group present), and ***angular*** (two nonbonding electron groups present). The molecules CH_4 (methane), NH_3 (ammonia), and H_2O (water) illustrate this sequence of molecular geometries:



Tetrahedral



Trigonal pyramidal



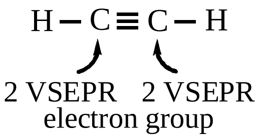
Angular

In all three molecules, the VSEPR electron groups arrange themselves at the corners of a tetrahedron. Again, note that the word used to describe the geometry of the molecule does not take into account the positioning of nonbonding electron groups.

3.7.4 Molecules with more than one central atom

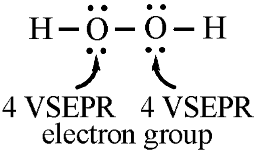
The molecular shape of molecules that contain more than one central atom can be obtained by considering each central atom separately and then combining the results. Let us apply this principle to the molecules C_2H_2 (acetylene), H_2O_2 (hydrogen peroxide), and HN_3 (hydrogen nitrogen), all of which have a four-atom "chain" structure. Their Lewis structures and VSEPR electron group counts are as follows:

Acetylene



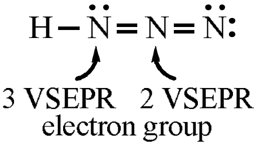
Linear C central

Hydrogen peroxide



Angular O central

Hydrogen nitrogen



Linear N central

3.8 Bond and molecular polarity

When two atoms of equal electronegativity share one or more pairs of electrons, each atom exerts the same attraction for the electrons, which results in the electrons being *equally* shared. This type of bond is called a nonpolar covalent bond. ***A nonpolar covalent bond*** is a covalent bond in which there is equal sharing of electrons between two atoms.

When the two atoms involved in a covalent bond have different electronegativities, the electron-sharing situation is more complex. The atom that has the higher electronegativity attracts the electrons more strongly than the other atom, which results in an unequal sharing of electrons. This type of covalent bond is called a polar covalent bond. ***A polar covalent bond*** is a covalent bond in which there is unequal sharing of electrons between two atoms.

The significance of unequal sharing of electrons in a polar covalent bond is that it creates fractional positive and negative charges on atoms. Although both atoms involved in a polar covalent bond are initially uncharged, the unequal sharing means that the electrons spend more time near the more electronegative atom of the bond (producing a fractional negative charge) and less time near the less electronegative atom of the bond (producing a fractional positive charge). The presence of such fractional charges on atoms within a molecule often significantly affects molecular properties.

Bond polarity is a measure of the degree of inequality in the sharing of electrons between two atoms in a chemical bond. The numerical value of the electronegativity difference between two bonded atoms gives an approximate measure of the polarity of the bond. The greater the numerical difference, the greater the inequality of electron sharing and the greater the polarity of the bond. As the polarity of the bond increases, the bond is increasingly ionic.

The existence of ***bond polarity*** means that there is no natural boundary between ionic and covalent bonding. Most bonds are a mixture of pure ionic and pure covalent bonds; that is, unequal sharing of electrons occurs. Most bonds have both ionic and covalent character. Nevertheless, it is still convenient to use the terms ***ionic*** and ***covalent*** in describing chemical bonds, based on the following arbitrary but useful (though not infallible) guidelines, which relate to electronegativity difference between bonded atoms.

1. Bonds that involve atoms with the same or very similar electronegativities are called ***non-polar covalent bonds*****.** "Similar" here means an electronegativity difference of 0.4 or less.

Technically, the only purely nonpolar covalent bonds are those between identical atoms. However, bonds with a small electronegativity difference behave very similarly to purely nonpolar covalent bonds.

2. Bonds with an electronegativity difference greater that 0.4 but less than 1.5 are called ***polar covalent bonds***.

3. Bonds with an electronegativity difference greater than 2.0 are called ***ionic bonds***.

4. Bonds with an electronegativity difference between 1.5 and 2.0 are considered *ionic* if the bond involves a metal and a nonmetal, and ***polar covalent*** if the bond involves two nonmetals. In the 1.5 – 2.0 range of electronegativity difference some

compounds exhibit characteristics associated with ionic compounds. This rule helps in dealing with this "borderline" area.

Molecules, as well as bonds, can have polarity. ***Molecular polarity*** is a measure of the degree of inequality in the attraction of bonding electrons to various locations within a molecule. In terms of electron attraction, if one part of a molecule is favored over other parts, then the molecule is polar. ***A polar molecule*** is a molecule in which there is an unsymmetrical distribution of electronic charge. In a polar molecule, bonding electrons are more attracted to one part of the molecule than to other parts. ***A nonpolar molecule*** is a molecule in which there is a symmetrical distribution of electron charge. Attraction for bonding electrons is the same in all parts of a non-polar molecule. Molecular polarity depends on two factors: bond polarities and molecular geometry. In molecules that are symmetrical, the effects of polar bonds may cancel each other, resulting in the molecule as a whole having no polarity.

Determining the molecular polarity of a diatomic molecule is simple because only one bond is present. If the bond is nonpolar then the molecule is nonpolar; if the bond is polar than the molecule is polar.

Determining molecular polarity for triatomic molecules is more complicated. Two different molecular geometries are possible: linear and angular. In addition, the symmetrical nature of the molecule must be considered.

Let us consider the polarities of three specific triatomic molecules: CO_2 (linear), H_2O (angular), and HCN (linear).

In the linear CO_2 molecule, both bonds are polar (oxygen is more electronegative than carbon). Despite the presence of these polar bonds, CO_2 molecules are nonpolar. The effects of the two polar bonds are canceled as a result of the oxygen atoms being arranged symmetrically around the carbon atom. The shift of electronic charge toward one oxygen atom is exactly compensated for by the shift of electronic charge toward the other oxygen atom. Thus one end of the molecule is not negatively charged relative to the other end (a requirement for polarity), and the molecule is nonpolar.

The nonlinear (angular) triatomic H_2O molecule is polar. The bond polarities associated with the two hydrogen-oxygen bonds do not cancel one another because of the nonlinearity of the molecule.

As a result of their orientation, both bonds contribute to an accumulation of negative charge on the oxygen atom. The two bond polarities are equal in magnitude but are not opposite in direction.

The generalization that linear triatomic molecules are nonpolar and nonlinear triatomic molecules are polar, which you might be tempted to make on the basis of our discussion of CO_2 and H_2O molecular polarities, is not valid. The linear molecule HCN, which is polar, invalidates this statement. Both bond polarities contribute to nitrogen's acquiring a partial negative charge relative to hydrogen in HCN.

Molecules that contain four and five atoms commonly have trigonal planar and tetrahedral geometries, respectively. Such molecules in which all of the atoms attached to the central atom are identical, such as SO_3 (trigonal planar) and CH_4 (tetrahedral), are *nonpolar*. The individual bond polarities cancel as a result of the highly symmetrical arrangement of atoms around the central atom.

If two or more kinds of atoms are attached to the central atom in a trigonal planar or tetrahedral molecule, the molecule is polar. The high degree of symmetry required for cancellation of the individual bond polarities is no longer present. For example, if one of the hydrogen atoms in CH_4 (a nonpolar molecule) is replaced by a chlorine atom, then a polar molecule results, even though the resulting CH_3Cl is still a tetrahedral molecule. A carbon-chlorine bond has a greater polarity than a carbon-hydrogen bond; chlorine has an electronegativity of 3.0, and hydrogen has an electronegativity of only 2.1.

CONCEPTS TO REMEMBER

Chemical bonds. Chemical bonds are the attractive forces that hold atoms together in more complex units. Chemical bonds result from the transfer of valence electrons between atoms (ionic bond) or from the sharing of electrons between atoms (covalent bond).

Valence electrons. Valence electrons, for representative elements, are the electrons in the outermost electron shell, which is the shell with the highest shell number. These electrons are particularly important in determining the bonding characteristics of a given atom.

Octet rule. In compound formation, atoms of representative elements lose, gain, or share electrons in such a way that their electron configurations become identical to those of the noble gas nearest them in the periodic table.

Ionic compounds. Ionic compounds commonly involve a metal atom and a nonmetal atom. Metal atoms lose one or more electrons, producing positive ions. Nonmetal atoms acquire the electrons lost by the metal atoms, producing negative ions. The oppositely charged ions attract one another, creating ionic bonds.

Charge magnitude for ions. Metal atoms containing one, two, or three valence electrons tend to lose such electrons, producing ions of +1, +2, or +3 charge, respectively. Nonmetal atoms containing five, six, or seven valence electrons tend to gain electrons, producing ions of −3, −2, or −1 charge, respectively.

Chemical formulas for ionic compounds. The ratio in which positive and negative ions combine is the ratio that causes the total amount of positive and negative charges to add up to zero.

Structure of ionic compounds. Ionic solids consist of positive and negative ions arranged in such a way that each ion is surrounded by ions of the opposite charge.

Molecular compounds. Molecular compounds usually involve two or more nonmetals. The covalent bonds within molecular compounds involve electron sharing between atoms. The covalent bond results from the common attraction of the two nuclei for the shared electrons.

Bonding and nonbonding electron pairs. Bonding electrons are pairs of valence electrons that are shared between atoms in a covalent bond. Nonbonding electrons are pairs of valence electrons about an atom that are not involved in electron sharing.

Types of covalent bonds. One shared pair of electrons constitutes a single covalent bond. Two or three pairs of electrons may be shared between atoms to give double and triple covalent bonds. Most often, both atoms of the bond contribute an equal number of electrons to the bond. In a few cases, however, both electrons of a shared pair come from the same atom; this is a coordinate covalent bond.

Number of covalent bonds formed. There is a strong tendency for nonmetals to form a particular number of covalent bonds. The number of valence electrons the nonmetal has and the number of covalent bonds it forms give a sum of eight.

Molecular geometry. Molecular geometry describes the way atoms in a molecule are arranged in space relative to one another. VSEPR theory is a set of procedures used to predict molecular geometry from a compound's Lewis structure. VSEPR theory is based on the concept that valence shell electron groups about an atom (bonding or nonbonding) orient themselves as far away from one another as possible (to minimize repulsions).

Electronegativity. Electronegativity is a measure of the relative attraction that an atom has for the shared electrons in a bond. Electronegativity values are useful in predicting the type of bond that forms (ionic or covalent).

Bond polarity. When atoms of like electronegativity participate in a bond, the bonding electrons are equally shared and the bond is non-polar. When atoms of differing electronegativity participate in a bond, the bonding electrons are unequally shared and the bond is polar. In a polar bond, the more electronegative atom dominates the sharing process. The greater the electronegativity differences between two bonded atoms, the greater the polarity of the bond.

Molecular polarity. Molecules as a whole can have polarity. If individual bond polarities do not cancel because of the symmetrical nature of a molecule, then the molecule as a whole is polar.

Binary molecular compound nomenclature. Names for binary molecular compounds usually contain numerical prefixes that give the number of each type of atom present per molecule in addition to the names of the elements.

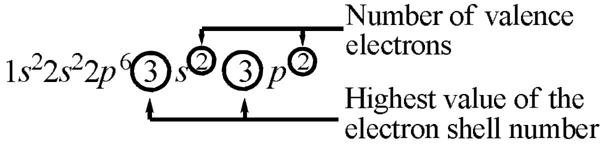
SAMPLE PROBLEMS WITH SOLUTIONS

Problem 1

Determine the number of valence electrons in ${}_{14}\text{Si}$.

Solution

Atoms of the element silicon have four valence electrons, as can be seen by examining silicon's electron configuration.



Electrons in two different subshells can simultaneously be valence electrons. The highest shell number is 3, and both the 3*s* and the 3*p* subshells belong to this shell. Hence all of the electrons in both of these subshells are valence electrons.

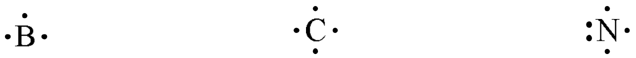
Problem 2

Write Lewis symbols for the B, C, N.

Solution

These elements are sequential elements in Period 2 of the periodic table; B is in Group IIIA (three valence electrons), C is in

Group IVA (four valence electrons), and N is in Group VA (five valence electrons). The Lewis symbols for these elements are:

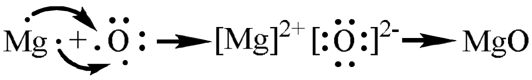


Problem 3

Show the formation of the magnesium oxide using Lewis structures.

Solution

Magnesium (a Group IIA element) has two valence electrons, and oxygen (a Group VIA element) has six valence electrons. The transfer of the two magnesium valence electrons to an oxygen atom results in each atom having a noble-gas electron configuration. Thus these two elements combine in a one-to-one ratio.

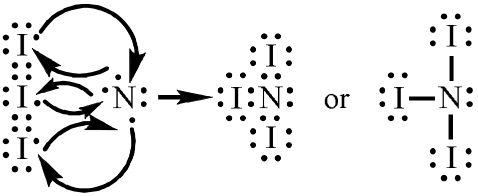


Problem 4

Draw Lewis structures for the simplest binary compounds that can be formed from the nitrogen and iodine.

Solution

Nitrogen is in Group VA of the periodic table and has five valence electrons. It will need to form three covalent bonds to achieve an octet of electrons. Iodine, in Group VIIA of the periodic table, has seven valence electrons and will need to form only one covalent bond in order to have an octet of electrons. Therefore, three iodine atoms will be needed to meet the needs of one nitrogen atom. The Lewis structure for this molecule is:



Problem 5

Consider the following bonds:

N – Cl, Ca – F, C – O, B – H, N – O.

A. Rank the bonds in order of increasing polarity.

B. Determine the direction of polarity for each bond. The period 2 alkaline earth metal.

C. Classify each bond as nonpolar covalent, polar covalent, or ionic.

Solution

First, the electronegativity difference for each of the bonds is calculated using the electronegativity values:

N – Cl	3.0 – 3.0 = 0.0
Ca – F	4.0 – 1.0 = 3.0
C – O	3.5 – 2.5 = 1.0
B – H	2.1 – 2.0 = 0.1
N – O	3.5 – 3.0 = 0.5

A. Bond polarity increases as electronegativity difference increases. Using the mathematical symbol <, which means “is less than,” we can rank the bonds in terms of increasing bond polarity as follows:

N – Cl < B – H < N – O < C – O < Ca – F

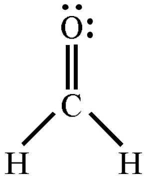
B. The direction of bond polarity is from the least electronegative atom to the most electronegative atom. The more electronegative atom bears the fractional negative charge (δ−).

C. Nonpolar covalent bonds require a difference in electronegativity of 0.4 or less, and an electronegativity difference of 2.0 or greater corresponds to ionic bonds. Bonds with an electronegativity difference greater than 0.4 but less than 1.5 are polar covalent. If the electronegativity difference is between 1.5 and 2.0, the bond is polar covalent if it involves two nonmetals, but is considered ionic if the bond involves a metal and a nonmetal. Using these guidelines the bond classifications are:

Nonpolar covalent: N – Cl, B – H
Polar covalent: N – O, C – O
Ionic: Ca – F

Problem 6

Predict the molecular geometry of formaldehyde using VSEPR theory.



Solution

Molecules with three VSEPR electron groups have two possible molecular structures: trigonal planar and angular. The former occurs when all three VSEPR electron groups are bonding and the latter when one of the three VSEPR electron groups is nonbonding.

The molecular geometry of is triangular planar.

INDIVIDUAL TEST PAPER

Exercise 1

Design electronic-graphic formulas of the elements given in the table 3.1 and explain the different valence of each element.

Table 3.1 – Variants of the problem

Variant	Elements and their valence	Variant	Elements and their valence
1	Sc(0, 2, 3), Ga(1, 3)	14	In(1, 3), Ag(1, 2, 3)
2	S(2, 4, 6), Al(1, 3)	15	Zr(0, 2, 3, 4), Pb(2, 4)
3	F(1), Cl(1, 3, 5, 7)	16	Ru(0, 2, 3, 6, 8) Cs(1)
4	Fe(0, 2, 3, 6), Ge(2, 4)	17	Ti(0, 2, 3, 4), Te(2, 4, 6)
5	Ti(0, 2, 3, 4), Ge(2, 4)	18	He(0), Xe(0, 2, 4, 6, 8)
6	Sn(2, 4), Zr(0, 2, 3, 4)	19	Hf(0, 2, 3, 4), C(2, 4)
7	Mn(0, 2, 3, 4, 6, 7), O(2)	20	W(0, 2, 3, 4, 6), Po(2, 4, 6)
8	V(0, 2, 3, 4, 5), As(3, 5)	21	Y(0, 2, 3), Br(1, 3, 5, 7)
9	Mo(0, 2, 3, 4, 6), Rb(1)	22	Te(2, 4, 6) Sc(0, 2, 3)
10	Re(0, 2, 3, 4, 6, 7), Sr(2)	23	At(1, 3, 5, 7), Cd(0, 2)
11	Se(2, 4, 6), P(3, 5)	24	Ti(0, 2, 3, 4), Si(2, 4)
12	Na(1), Cu(1, 2, 3)	25	H(1), Br(1, 3, 5, 7)
13	N(3, 4), Cr(0, 2, 3, 4, 6)	26	Ag(1, 2, 3), Au(1, 2, 3)

Exercise 2

Range the compounds (table 3.2) in series in which the polarity of a bond will decrease using the values of electronegativity of atoms.

Table 3.2 – Variants of the problem

Variant	Chemical compounds	Variant	Chemical compounds
1	SiH_4, CCl_4, GeF_4, CO	14	$TiCl_4$, ZrI_4, HfF_4, $HfCl_4$
2	ScF_3, PCl_3, $MgCl_2$, NH_3	15	Sc_2O_3, YCl_3, La_2O_3, NO
3	LiCl, MgO, Na_2O, LiH	16	VCl_3, TaI_3, $NbCl_3$, VF_3
4	KCl, NaF, K_2O, Na_2S	17	BF_3, Al_2O_3, $AlCl_3$, B_2O_3
5	PH_3, NCl_3, Na_3P, PBr_3	18	GaAs, ClF_3, $BrCl_3$, IF_3
6	CaI_2, MgF_2, CaH_2, CaO	19	SO_2, SeF_4, $TeCl_4$, PoO_2
7	$TiCl_2$, ZrO, TiS, HfF_2	20	CO_2, CCl_4, GeI_4, SnO_2
8	Na_2O, KF, K_2S, NaH	21	CdS, ZnO, $HgCl_2$, ZnI_2
9	CaO, HCl, NH_3, CCl_4	22	$AlCl_3$, Ga_2O_3, $InCl_3$, TlI_3
10	PH_3, H_2O, AsF_3, H_2Se	23	PF_3, $AsCl_3$, SbI_3, $BiCl_3$
11	Al_2O_3, In_2S_3, Al_2Se, OF_2	24	CrO, $CrCl_2$, MoI_2, WO_3
12	Ba_3N_2, $CaCl_2$, BaF_2, KI	25	CCl_4, SiF_4, GeI_4, SnO_2
13	$MnCl_2$, NiF_2, $FeCl_2$, HF	26	PH_3, $TiCl_2$, Al_2O_3, GaAs

Exercise 3

Predict the geometry of chemical particles given in the table 3.3, using VSEPR theory.

Table 3.3 – Variants of the problem

Variant	Chemical particles	Variant	Chemical particles
1	BeH_2, CH_4, AlH_3	6	CO_3^{2-}, $GeCl_4$, $BeCl_2$
2	SiH_4, BCl_3, MgH_2	7	CF_4, SiO_3^{2-}, $MgCl_2$
3	CaH_2, AlF_3, GeH_4	8	$CaCl_2$, C_2H_4, SiF_4
4	SrH_2, CCl_4, BF_3	9	GeF_4, HCOH, $SrCl_2$
5	BaH_2, $SiCl_4$, BCl_3	10	C_2H_6, $BaCl_2$, Na_3B

Continued of table 3.3

Variant	Chemical particles	Variant	Chemical particles
11	$PbCl_4$, $GaCl_3$, CO_2	19	GeF_4, HgF_2, $InBr_3$
12	SiO_2, SnF_4, GaF_3	20	ZnF_2, HCOOH,
13	$InCl_3$, PbF_4, $HgCl_2$	21	$Ge(OH)_4$, CH_3COOH,
14	$ZnCl_2$, InF_3, CF_4	22	$C_2H_2Cl_2$, GeO_2, Li_3B
15	SiF_4, $GaBr_3$, $CdCl_2$	23	$PbCl_4$, BeH_2,
16	C_2H_5OH, K_3B, C_2H_2	24	SnO_2, $SnBr_4$, GaH_3
17	CH_3OH, SnO_3^{2-}, C_2Cl_2	25	GeI_4, PbO_2, HCOONa
18	CS_2, CH_3COH, $SnCl_4$	26	$MgCl_2$, SnI_4, AlF_3

CHAPTER 4 Chemical thermodynamics and kinetics

4.1 Thermodynamic potentials

Internal energy and first law of thermodynamics. The energy change of a system ΔU is equal to the heat absorbed by the system *Q* plus the work done by the system. The reason for the minus sign for work *A*, is that any work done by the system results in a loss of energy for the system as a whole,

$$\Delta U = Q - A \qquad (4.1)$$

where, U – internal energy of the system;
Q – heat absorbed by the system;
A – work done by the system.

Making a substitution for work, the equation can be expressed as:

$$\Delta U = Q - p\Delta V \qquad (4.2)$$

For constant volume, the equation becomes: $\Delta U = Q_V$

Enthalpy and Hess' law. Enthalpy *H* is the heat content of the system at constant pressure. It is a thermodynamic quantity that equal to:

$$H = U + pV \qquad (4.3)$$

where, U – is the thermal energy;
p – is pressure;

V – is volume.

If the pressure is constant and no other work is done other than $p\Delta V$ work, then the increase in enthalpy is equal to the heat absorbed at constant pressure $\Delta H = Q_p$. Thus:

$$Q_p = \Delta U + p\Delta V$$

$$Q_p = (U_2 - U_1) + p(V_2 - V_1)$$

$$Q_p = (H_2 - H_1) = \Delta H$$

If $\Delta H < 0$, the process is regarded as exothermic;
if $\Delta H > 0$, the process is regarded as endothermic.

The amount of heat generated by a reaction is the same whether the reaction takes place in one step or in several steps. Hence, ΔH values (and, thus, ΔG values) are additive. This law, also known as the law of constant heat summation or ***Hess' law***, was the earliest example of the additivity principle, which also states that ΔG values are additive.

The final value of ΔH for the overall process is the sum of all the enthalpy changes.

$$\Delta H^o = \sum n\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reactants}) \qquad (4.4)$$

Entropy. Entropy S [J/K] is a fundamental thermodynamic state function, and as such, not dependent on the path by which a particular state is reached. For a reversible process, the differential change in entropy, dS, is equal to the amount of energy absorbed by the system, dQ, divided by the absolute temperature, T. Thus,

$$\Delta S = \int_1^2 \frac{dQ}{T}$$

If irreversibility occurs at any point in the process under consideration, then $\Delta S > \frac{dQ}{T}$. The entropy of an isolated system undergoing an irreversible process always increases (in other words, for any isolated system $\Delta S \geq 0$). Entropy is the measure of the degree of randomness of a system.

Gibbs free energy. A fundamental thermodynamic parameter (typically symbolized by G) used to describe the thermodynamic driving forces governing a closed system(s) at constant temperature and pressure. The Gibbs free energy is a state function that equates the enthalpy H minus the absolute temperature T multiplied by the entropy, S. Thus,

$$G = H - TS \tag{4.5}$$

The Helmholtz energy F and the Gibbs energy G are related by the expression: $G = F + pV$. In a closed system at constant temperature and pressure, where in only pV work is permitted, the system at equilibrium will have a minimum value for the Gibbs free energy.

Gibbs free energy is the amount of energy available to the system to do useful work:

$$\Delta G = \Delta H - T\Delta S \tag{4.6}$$

If $\Delta G < 0$ spontaneous process from $1 \rightarrow 2$;
if $\Delta G > 0$ spontaneous process from $1 \leftarrow 2$;
if $\Delta G = 0$ chemical equilibrium.

4.2 Basic concepts of chemical kinetics

Reaction order and molecularity. In the context of reaction rate equations, one can identify systems obeying the following mathematical forms (Fig. 4.1):

Zero Order	$v = k_0$
First Order	$v = k_1[\mathrm{A}]$
Second Order	$v = k_2[\mathrm{A}]^2$ or $v = k[\mathrm{A}][\mathrm{B}]$
Third Order	$v = k_3[\mathrm{A}]^3$ or $v = k[\mathrm{A}]^2[\mathrm{B}]$ or $v = k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$

where, the respective units of k_0, k_1, k_2, and k_3 are $\mathrm{M{\cdot}s^{-1}}$, $\mathrm{s^{-1}}$, $\mathrm{M^{-1}{\cdot}s^{-1}}$, and $\mathrm{M^{-2}{\cdot}s^{-1}}$.

These expressions and the units of their rate constants all express reaction rate as a molarity change per unit time (i.e., $-d[\mathrm{X}]/dt$). Note also that, while we list a third order reaction above, no such processes are known to occur for chemical reactions in the liquid phase.

The functional nature of some rate equations requires that rate constants occasionally can be of a mixed order, (i.e., they can have nonintegral dimensions with respect to reactant molarity). Whether the reaction order is an integer or a fractional value, its value n is obtained from the slope of a plot of reaction rate versus $\log_{10}$ [Reactant].

Another term used to describe rate processes is ***"molecularity,"*** which can be defined as an integer indicating the molecular stoichiometry of an elementary reaction, which is a one-step reaction. Collision theory treats molecularity in terms of the number of molecules (or atoms, if one or more of the reacting entities are single atoms) involved in a simple collisional process that ultimately leads to product formation. Transition-state theory considers molecularity as the number of molecules (or entities) that are used to form the activated complex. For reactions in solution, solvent molecules are counted in the molecularity, only if they enter into the overall process and not when they merely exert an environmental or solvent effect.

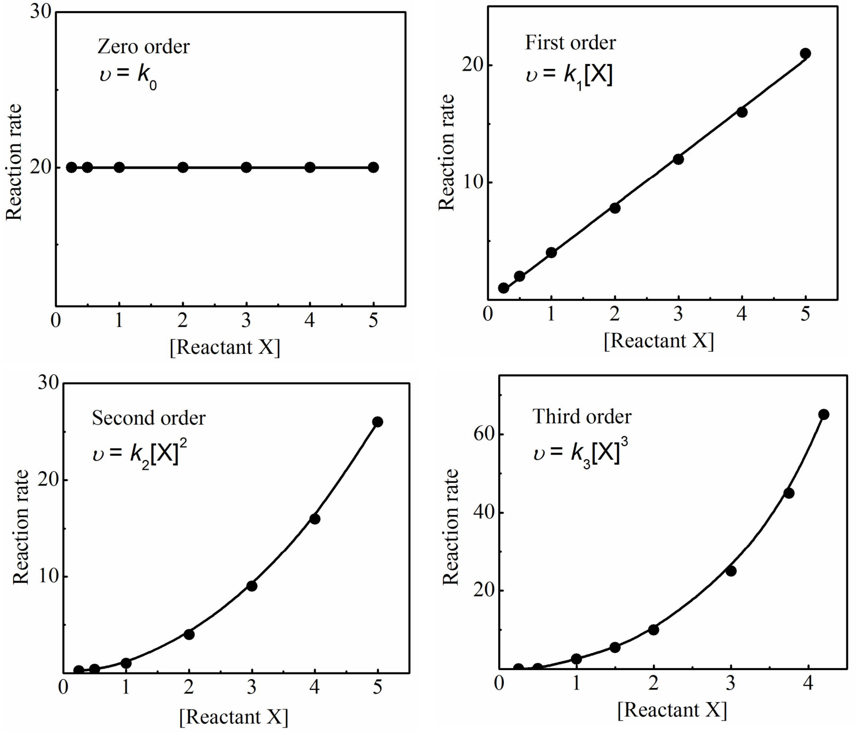


Fig. 4.1 – Concentration dependency of zero-, first-, second-, and third- order chemical reactions.

Again, the molecularity of a reaction is always an integer and only applies to elementary reactions. Such is not always the case for the order of a reaction. The distinction between molecularity and order can also be stated as follows: molecularity is the theoretical description of an elementary process; reaction order refers to the entire empirically derived rate expression (which is a set of elementary reactions) for the complete reaction. Usually a bimolecular reaction is second order; however, the converse need not always be true. Thus, unimolecular, bimolecular, and termolecular reactions refer to elementary reactions involving one, two, or three entities that combine to form an activated complex.

First order processes. In a first order reaction, the rate is directly proportional to the concentration of reactant, as indicated by the following rate law:

$$\nu = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}] \qquad (4.7)$$

Rearranging this expression allows one to separate variables to form:

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]} = kdt$$

where the concentration of A at time t is $[\mathrm{A}]_t$ and that originally present is $[\mathrm{A}]_0$. Integration of the above equation yields:

$$[\mathrm{A}]_\mathrm{t} = [\mathrm{A}]_0 \exp(-kt)$$

The half-life of a first-order process (i.e., the time $t_{1/2}$ required for $[\mathrm{A}]_0$ to decay to $0.5[\mathrm{A}]_0$) is given as:

$$\ln 2 = 0.693 = kt_{1/2} \text{ or } \log 2 = kt_{1/2} / 2.30$$

These equations tell us that at successive time intervals equal to $n X t_{1/2}$ where n = 1,2,3, etc.), the concentration of A will fall to 0.50, 0.25, 0.125, etc., of the original amount of A (Fig. 4.2).

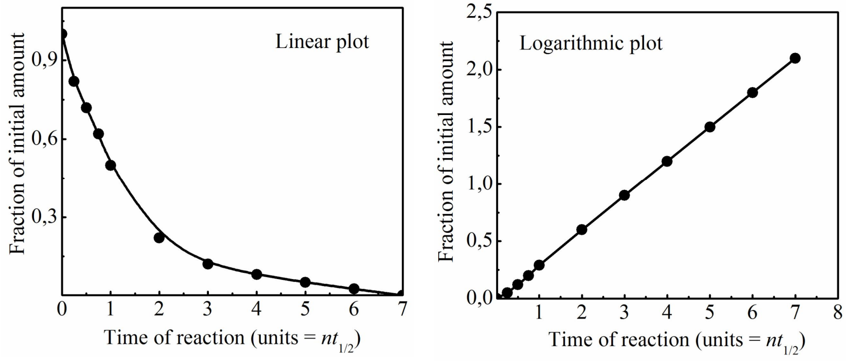


Fig 4.2 – Graphical representations of a first-order rate process.

First-order reaction kinetics is frequently observed in organic chemistry in the form of an S_N1 reaction, indicating it is a first-order nucleophilic substitution type. An example is the solvolysis of tert-butylbromide at alkaline pH to form tert-butanol and bromide ion. The reaction probably proceeds in two steps:

$$A \xrightarrow{siowest} B \xrightarrow{fastest} C$$

The first-order nature of this reaction reminds us that rate-limiting hydroxide attack on tert-butylbromide is not a feature of this S_N1 reaction.

Bimolecular rate processes. Many chemical processes involve the rate-limiting reaction of two components:

$$A + B \xrightarrow{k} C$$

where, k has units equal to $M^{-1}s^{-1}$.

The differential equation for a bimolecular rate process can be written as:

$$\nu = \frac{dx}{dt} = k[\mathrm{A}][\mathrm{B}] = k(a - x)(b - x)$$

where, *a* equals the initial reactant A concentration;

b equals the initial reactant B concentration;

x equals the amount of product at time t;

(a –x) equals the concentration of A at time *t;*

(b – x) equals the concentration of B at time *t.*

After separating variables, we get:

$$\frac{dx}{\{(a - x)(b - x)\}} = kdt$$

After integration by the method of partial fractions, the result is:

$$\frac{\ln(a - x) - \ln(b - x)}{a - x} = kt + \text{constant}$$

where, the constant of integration equals $\ln\{(a/b)/(a - b)\}$ at $t = 0$ and $x = 0$. This yields the integrated second-order rate law $(a \neq b)$:

$$\frac{1}{a - b}\ln\frac{b(a - x)}{a(b - x)} = kt$$

Transition state theory. Arrhenius and Van't Hoff independently proposed that the rate constant for a chemical reaction must depend on the absolute temperature *T,* thereby transforming the empirical relationship:

$$k = \mathrm{A}\, e^{-\frac{\mathrm{B}}{T}}$$

where, A and B are suitably chosen constants into a related form:

$$k = \mathrm{A}\, e^{-\frac{\Delta E}{RT}}$$

where, R = 8.31 J/mol·K is the universal gas constant

This equation is widely known as the Arrhenius Law, and the preexponential term is known as the frequency factor (with the same units as k).

The constant A, in many respects, is analogous to the highest achievable magnitude of the rate constant k, and the $e^{-\frac{\Delta E}{RT}}$ term defines the fraction of molecules having sufficient energy to react.

If $\Delta E \approx 0$, then $e^{-\frac{\Delta E}{RT}} \approx e^0$, which equals unity; thus, $k \approx$ A. On the other hand, if ΔE is very large, such that $E \sim 20RT$, then $e^{-\frac{\Delta E}{RT}} \sim e^{-20}$, which is approximately $2\cdot10^{-9}$; therefore, k is extremely small in this example. This behavior obeys the Boltzmann principle which states that the fraction of collisions with energy exceeding a threshold value of ΔE is $e^{-\frac{\Delta E}{RT}}$. This fraction, also known as the Boltzmann factor, is greater: (a) as the absolute temperature T becomes greater or (*b*) as ΔE becomes smaller.

The Arrhenius equation can be rearranged to yield the following expression:

$$\ln k = \ln \mathrm{A} - \frac{\Delta E}{RT}$$

If a process obeys the Arrhenius law, then a plot of ln$k$ versus T^{-1} should yield a straight line with a slope of $-(\Delta E/R)$. This indicates that ΔE represents a barrier to reactivity, perhaps related to organizational events that reflect the conversion of the reactant to an activated species.

Eyring and Polanyi extended the Arrhenius concept concerning the nature of barriers to chemical reactivity. They considered the concept of a transition state which can be defined as the highest energy species or configuration in a chemical reaction. Transition-state theory now forms the basis of uncatalyzed and catalyzed chemical reactions, whether homogeneous, heterogeneous, or interfacial processes (see below). The simplest schematic representation is:

$$\mathrm{A + B \leftrightarrow X^{\neq} \rightarrow Products}$$

where, $X^{\neq}$ is the activated transition-state (TS) complex in the transition state. We deliberately treat the system as the simplest two-step process here (Fig. 4.3).

4.3 Chemical equilibrium

Homogeneous and heterogeneous equilibrium. Chemical equilibrium is a condition of balance in a chemical system, at which no further change in reactant and product concentrations occurs. If actions occurring within the reaction result in no net change in the reactant and product concentrations, the system is said to be in dynamic equilibrium. A chemical equilibrium is a dynamic equilibrium when the reaction rate in the forward direction is balanced by the rate in the reverse direction. The potential energy of a system reaches a minimum when a system is at equilibrium. If the potential energy is at a maximum, the system’s state is said to be unstable or metastable.

$$A{-}B + C \rightarrow A + B{-}C$$

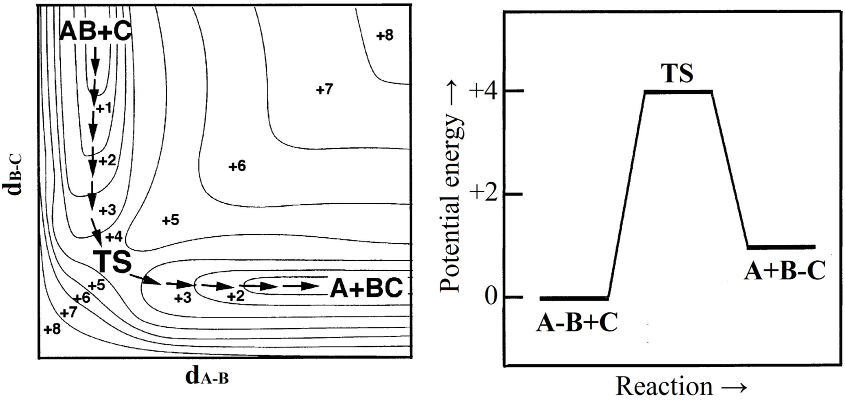


Fig. 4.3 – Energetics of a bimolecular rate process.

Top: Representation of the potential energy surface along coordinate axes corresponding to the interatomic distance of B-to-C and A-to-B, where incremental displacements along the potential energy axis are shown as a series of isoenergetic lines (each marked by arbitrarily chosen numbers to indicate increased energy of the transition-state (TS) intermediate relative to the reactants).

Bottom: Typical reaction coordinate diagram for a bimolecular group transfer reaction.

Homogeneous equilibrium occurs when all reacting species are in the same phase. For the general reaction:

$$aA + bB \leftrightarrow cC + dD \qquad (4.8)$$

The equation expressing the law of mass action at equilibrium is:

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \qquad (4.9)$$

The quantity K_c, is a constant, called the equilibrium constant (in this case it denotes the equilibrium constant for species in solution, expressed as moles per liter). The magnitude of K_c tells us to what extent the reaction proceeds. A large K_c indicates that the reactions proceeds to the right of the reaction. A low value indicates that the reaction proceeds to the right of the reaction.

For gas-phase equilibrium the expression becomes:

$$K_p = \frac{p_{\mathrm{C}}^{\mathrm{c}} p_{\mathrm{D}}^{\mathrm{d}}}{p_{\mathrm{A}}^{\mathrm{a}} p_{\mathrm{B}}^{\mathrm{b}}} \qquad (4.10)$$

where, p is the partial pressures of the species in the reaction.

Heterogeneous equilibrium involves reactants and products in different phases. For example, when calcium carbonate is heated in a closed vessel the following equilibrium reaction occurs:

$$CaCO_3(s) \rightarrow CaO\ (s) + CO_2(g) \qquad (4.11)$$

The reactant is a solid, while the products arc in the solid and gas phase. The equilibrium expression is written as the following:

$$K_c^* = \frac{[\mathrm{CaO}][\mathrm{CO_2}]}{[\mathrm{CaCO_3}]} \qquad (4.12)$$

In any reaction that includes a solid, the solid concentration will remain constant and therefore is not included in the equilibrium expression. The equilibrium expression now becomes:

$$K_{\mathrm{c}} = [CO_2] \qquad (4.13)$$

Le Chatelier's Principle. Le Chatelier's Principle states that when a system is in equilibrium and there is a change in one of the factors which affect the equilibrium > the system reacts in such a way as to cancel out the change and restore equilibrium.

An increase in temperature will shift the reaction in the direction of heat absorption.

An increase in the pressure will shift the reaction in the direction in which the number of moles is decreased. An increase or decrease in pressure does not affect a reaction in which there is no variation in the number of moles.

An increase in the concentration of one of the components will cause the reaction to shift so as to decrease the added component.

CONCEPTS TO REMEMBER

Thermodynamic equilibrium. State of a system at which no measurable changes of its intensive properties occur and no measurable flow of matter or energy takes place during the period of observation.

Heterogeneous system. System consisting of phases that are homogeneous systems and phase boundaries at which the intensive properties show discontinuities.

Homogeneous system. System of which all intensive properties are continuous functions of position throughout the system.

Enthalpy (H) – a thermodynamic function, especially useful when dealing with constant-pressure processes, defined by:

$$H = U + pV$$

where, U – is the thermal energy; p – is pressure; V – is volume.

Enthalpy of combustion – the enthalpy change in a combustion reaction. Its negative is the heat released in combustion.

Enthalpy of formation, standard – the enthalpy change for the reaction in which a substance is formed from its constituent elements, each in its standard reference state (normally refers to 1 mol, sometimes to 1 g, of the substance).

Entropy (S) – A thermodynamic function defined such that when a small quantity of heat dQ is received by a system at temperature T, the entropy of the system is increased by dQ/T, provided that no irreversible change takes place in the system.

Gibbs energy (G) – an important function in chemical thermodynamics, defined by:

$$G = H - TS$$

where, H – is the enthalpy, S – is the entropy, T – is the thermodynamic temperature.

Sometimes called Gibbs free energy and, in older literature, simply “free energy”.

Equilibrium constant (K_a) for a chemical reaction:

$$\mathrm{aA + bB \leftrightarrow cC + dD}$$

the equilibrium constant is defined by:

$$K_a = \frac{a_{\mathrm{C}}^{\mathrm{c}} a_{\mathrm{D}}^{\mathrm{d}}}{a_{\mathrm{A}}^{\mathrm{a}} a_{\mathrm{B}}^{\mathrm{b}}}$$

where, a_{i} – is the activity of component i. To a certain approximation, the activities can be replaced by concentrations. The equilibrium constant is related to $\Delta\mathrm{r}G^{o}$, the standard Gibbs energy change in the reaction, by $RT \ln K = -\Delta\mathrm{r}G^{\mathrm{o}}$.

Activation energy – in general, the energy that must be added to a system in order for a process to occur, even though the process may already be thermodynamically possible. In chemical kinetics, the activation energy is the height of the potential barrier separating the products and reactants. It determines the temperature dependence of the reaction rate.

Arrhenius equation – a key equation in chemical kinetics which expresses the rate constant k as $k = A\exp(-E_{\mathrm{a}}/RT)$, where $E\mathrm{a}$ is the activation energy, R the molar gas constant, and T the temperature. A is called the preexponential factor and, for simple gas phase reactions, may be identified with the collision frequency.

SAMPLE PROBLEMS WITH SOLUTIONS

Problem 1

Calculate the free energy change for the complete combustion of one mole of methane, CH_4(g), the main component of natural gas. Is this reaction spontaneous?

Solution

We begin by writing the equation that represents this reaction. Recall that "complete combustion" or burning, is a reaction with oxygen from the atmosphere, forming carbon dioxide and water:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$$

Now we apply equation:

$$\Delta G^o = \sum n\Delta_f G^o(\text{products}) - \sum n\Delta_f G^o(\text{reactants})$$

and then consult a table of thermodynamic values:

ΔG^o = (1 mol)[Δ_f G^o for CO_2(g)] + (2 mol)[Δ_f G^o for H_2O(l)] – (1 mol)[Δ_f G^o for CH_4(g)] – (2 mol)[Δ_f G^o for O_2(g)] = = (1 mol)[–394.4 kJ/mol] + (2 mol)[–237.0 kJ/mol] – (1 mol) [–50.8 kJ/mol] – (2 mol)[0 kJ/mol] = –817.2 kJ/mol

The negative value of $\Delta G°$ indicates that the reaction is spontaneous. This matches our experiences in everyday life, where we have seen that natural gas burns spontaneously.

Problem 2

Determine the standard entropy change for the decomposition of one mole of solid calcium carbonate, forming solid calcium oxide and carbon dioxide gas:

Solution

This is a straight-forward application of equation:

$$\Delta S^o = \sum n\Delta_f S^o(\text{products}) - \sum n\Delta_f S^o(\text{reactants})$$

followed by substitution of the appropriate values from a table.

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

ΔS^o = (1 mol)[Δ_f S^o for CaO(s)] + (1 mol)[Δ_f S^o for CO_2(g)] – (1 mol)[Δ_f S^o for $CaCO_3$(s)] = (1 mol)[38.1 J/mol·K] + (1 mol) [213.7 J/mol·K] – (1 mol)[92.6 J/mol·K] = 159.2 J/mol·K

Problem 3

Calculate Δ*G*° for the reaction in problem 2, the decomposition of calcium carbonate, from Δ*H*° and Δ*S*° values.

Solution

We have already calculated Δ*S*° for the reaction

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

as 160.6 J/ mol·K. We can find Δ*H*° for the reaction in a similar manner:

ΔH^o = (1 mol)[$\Delta_f\ H^o$ for CaO(s)] + (1 mol)[$\Delta_f\ H^o$ for CO_2(g)] – (1 mol)[$\Delta_f H^o$ for $CaCO_3$(s)] = (1 mol)[–635.1 kJ/mol] + + (1 mol)[–393.5 kJ/mol] – (1 mol)[–1207.0 kJ/mol] = 178.4 kJ/mol

Now we use equation 4.6 to find the value of Δ*G*°*:*

$\Delta G° = \Delta H° - T\Delta S° = 178.2 - 298 \cdot 160.6 = 130.9$ kJ/mol.

Notice that we used 298.15 K, or 25°C as the value of T. This is thermodynamic standard temperature. Also note how the Δ*S*° value was in joules per kelvin, while the Δ*H*° value was in kJ/mol. The J ↔ kJ conversion must be accounted for in the calculation.

Problem 4

In a reaction 2A → product the concentration of A decreases from 0.5 mol/l to 0.4 mol/l in 10 minutes. Calculate the rate during this interval.

Solution

$$\text{Rate} = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{2}\frac{(0.5-0.4)}{10} = -0.005$$

Negative sign simply indicates the fall in concentration of A. Thus, the rate of the reaction is 0.005 mol/l·min.

INDIVIDUAL TEST PAPER

Exercise 1

Complete a chemical reaction aA + bB + cC = dD + fF +gG from substances disposed in A, B, C, D, F, G columns of your variant in table 4.1 and then:

- Determine changes in the reaction enthalpy and entropy under standard conditions (ΔH^o, ΔS^o) using reference data (application A). Is this reaction exothermic or endothermic?
- Calculate the Gibbs Energy change under standard conditions ΔG^0. Is given reaction a spontaneous?

Table 4.1 – Variants of the problem

Variant	A	*n*, mol	B	C	D	F	G
1	$Mn_{(s)}$	0,12	$H_2O_{(l)}$	–	$Mn(OH)_{2(s)}$	$H_{2(g)}$	–
2	$Be_{(s)}$	1,23	$H_2SO_{4(l)}$	–	$BeO_{(s)}$	$S_{(s)}$	$H_{2(g)}$
3	$Ni_{(s)}$	0,75	$H_2O_{(l)}$	O_2	$Ni(OH)_{2(s)}$	–	–
4	$Sn_{(s)}$	3,40	$HNO_{3(l)}$	–	$Sn(NO_3)_{2(l)}$	$NO_{(g)}$	$H_2O_{(l)}$
5	$Be(NO_3)_{2(s)}$	2,84	–	–	$BeO_{(s)}$	$NO_{2(g)}$	$O_{2(g)}$
6	$Cu_{(s)}$	1,69	$HCl_{(l)}$	O_2	$CuCl_{2(l)}$	$H_2O_{(l)}$	–
7	$Si_{(s)}$	0,91	$NaOH_{(l)}$	$H_2O_{(l)}$	$Na_2SiO_{3(s)}$	$H_{2(g)}$	–
8	$Zn_{(s)}$	2,54	$H_2O_{(l)}$	–	$Zn(OH)_{2(s)}$	$H_{2(g)}$	–
9	$Ag_{(s)}$	3,05	$HNO_{3(l)}$	–	$AgNO_{3(s)}$	$NO_{2(g)}$	$H_2O_{(l)}$
10	$PbSO_{4(s)}$	1,82	$H_2O_{(l)}$	–	$H_2SO_{4(l)}$	$PbO_{2(s)}$	$Pb_{(s)}$
11	$Co_{(s)}$	2,56	$H_2O_{(l)}$	–	$Co(OH)_{2(s)}$	$H_{2(g)}$	–
12	$Pb_{(s)}$	0,48	$HNO_{3(l)}$	–	$Pb(NO_3)_{2(l)}$	$NO_{2(g)}$	$H_2O_{(l)}$
13	$Sb_{(s)}$	3,15	$HNO_{3(l)}$	–	$Sb_2O_{5(s)}$	$NO_{2(g)}$	$H_2O_{(l)}$

14	$Hg_{(l)}$	1,63	$HNO_{3(l)}$	$HCl_{(l)}$	$HgCl_{2(s)}$	$NO_{(g)}$	$H_2O_{(l)}$
15	$ZnS_{(s)}$	2,78	O_2	–	$SO_{2(g)}$	$H_2O_{(l)}$	–
16	$PH_{3(g)}$	0,17	O_2	–	$P_2O_{5(s)}$	$H_2O_{(l)}$	–

Continued of Table 4.1

Va-riant	A	*n*, mol	B	C	D	F	G
17	$Bi_{(s)}$	3,19	$HNO_{3(l)}$	–	$Bi(NO_3)_{3(l)}$	$NO_{2(g)}$	$H_2O_{(l)}$
18	$Cu_{(s)}$	1,08	$H_2O_{(l)}$	O_2	$Cu(OH)_{2(s)}$	–	–
1	2	3	4	5	6	7	8
19	$Cd_{(s)}$	2,71	$HNO_{3(l)}$	–	$Cd(NO_3)_{2(l)}$	$NO_{2(g)}$	$H_2O_{(l)}$
20	$Sn(NO_3)_{2(s)}$	3,66	–	–	$SnO_{(s)}$	$NO_{2(g)}$	O_2
21	$Ag_{(s)}$	0,42	$H_2S_{(g)}$	O_2	$Ag_2S_{(s)}$	$H_2O_{(l)}$	–
22	$Mn_{(s)}$	4,14	$HCl_{(l)}$	O_2	$MnCl_{2(s)}$	$H_2O_{(l)}$	–
23	$Cd_{(s)}$	2,92	$HCl_{(l)}$	O_2	$CdCl_{2(s)}$	$H_2O_{(l)}$	–
24	$Pb_{(s)}$	1,38	$H_2O_{(l)}$	O_2	$Pb(OH)_{2(s)}$	–	–
25	$Fe_{(s)}$	3,84	$HNO_{3(l)}$	–	$Fe(NO_3)_{3(l)}$	$NO_{(g)}$	$H_2O_{(l)}$
26	$Au_{(s)}$	0,72	$HCl_{(l)}$	O_2	$AuCl_{3(s)}$	$H_2O_{(l)}$	–

Exercise 2

Complete a chemical reaction $aA+bB$ □ $cC+dD$ from substances disposed in A, B, C, D columns of your variant in table 4.2.:

- Write the rate equations for forward and reverse reactions according to the law of acting mass.
- Calculate the equilibrium constant if the equilibrium concentration of each substance is 0.5 mol/l.
- Indicate the mode of changes in systems parameters (temperature, pressure, reactants and products concentrations) to

shift equilibrium in the direction of forward reaction (extent of a reaction).

Table 4.2 – Variants of the problem

Variant	Substances taking part in the reaction				$\Delta H°$, kJ/mol
	A	*B*	*C*	*D*	
1	$CO_{(g)}$	$Cl_{2(g)}$	$COCl_{2(g)}$	–	–109,8
2	$PCl_{5(g)}$	–	$PCl_{3(g)}$	$Cl_{2(g)}$	78,9
3	$SO_{2(g)}$	$O_{2(g)}$	$SO_{3(g)}$	–	–198,4
4	$H_{2(g)}$	$I_{2(g)}$	$HI_{(g)}$	–	–8,69
5	$CO_{2(g)}$	$C_{(s)}$	$CO_{(g)}$	–	172,5
6	$CH_{4(g)}$	$O_{2(g)}$	$H_{2(g)}$	$CO_{(g)}$	–71,2
7	$ICl_{(g)}$	–	$I_{2(s)}$	$Cl_{2(g)}$	34,8
8	$CO_{(g)}$	$Fe_2O_{3(s)}$	$FeO_{(s)}$	$CO_{2(g)}$	49,6
9	$NH_{3(g)}$	$O_{2(g)}$	$NO_{(g)}$	$H_2O_{(g)}$	–906,2
10	$CO_{(g)}$	$O_{2(g)}$	$CO_{2(g)}$	–	–565,9
11	$C_2H_5OH_{(l)}$	$O_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	–1234,9
12	$CH_{4(g)}$	$O_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	–802,2
13	$HCl_{(g)}$	$O_{2(g)}$	$Cl_{2(g)}$	$H_2O_{(g)}$	–116,8
14	$C_2H_{6(g)}$	–	$C_2H_{4(g)}$	$H_{2(g)}$	142,0
15	$SO_{2(g)}$	$NO_{2(g)}$	$SO_{3(g)}$	$NO_{(g)}$	–41,9
16	$CH_{4(g)}$	$Cl_{2(g)}$	$CH_3Cl_{(g)}$	$HCl_{(g)}$	–98,9
17	$CO_{(g)}$	$FeO_{(s)}$	$Fe_{(s)}$	$CO_{2(g)}$	–18,2
18	$CO_{(g)}$	$H_2O_{(g)}$	$CO_{2(g)}$	$H_{2(g)}$	–40,9
19	$CH_{4(g)}$	$CO_{2(g)}$	$CO_{(g)}$	$H_{2(g)}$	247,4
20	$NO_{(g)}$	$H_{2(g)}$	$H_2O_{(g)}$	$N_{2(g)}$	–664,5
21	$CH_{4(g)}$	$H_2O_{(g)}$	$CO_{(g)}$	$H_{2(g)}$	250,2

22	$H_{2(g)}$	$GeO_{2(s)}$	$Ge_{(s)}$	$H_2O_{(g)}$	–16,9
23	$F_{2(g)}$	$H_2O_{(l)}$	$HF_{(l)}$	$O_{2(g)}$	–708,7
24	$NO_{2(g)}$	$CO_{(g)}$	$CO_{2(g)}$	$NO_{(g)}$	–225,7

CHAPTER 5 Solution chemistry

5.1 General properties of solutions. Solubility

All samples of matter are either ***pure substances*** or ***mixtures***. Pure substances are of two types: ***elements*** and ***compounds***. Mixtures are of two types: ***homogeneous*** (uniform properties throughout) and ***heterogeneous*** (different properties in different regions).

A solution is a homogeneous mixture of two or more substances with each substance retaining its own chemical identity. ***A solvent*** is the component of a solution that is present in the greatest amount. A solvent can be thought of as the medium in which the other substances present are dissolved. ***A solute*** is a component of a solution that is present in a lesser amount relative to that of the solvent.

The general properties of a solution are as follows:

1. A solution contains two or more components: a solvent (the substance present in the greatest amount) and one or more solutes.

2. A solution has a variable composition; that is, the ratio of solute to solvent may be varied.

3. The properties of a solution change as the ratio of solute to solvent is changed.

4. The dissolved solutes are present as individual particles (molecules, atoms, or ions). Intermingling of components at the

particle level is a requirement for homogeneity.

5. The solutes remain uniformly distributed throughout the solution and will not settle out with time. Every part of a solution has exactly the same properties and composition as every other part.

6. The solute(s) generally can be separated from the solvent by physical means such as evaporation.

Solubility is the maximum amount of solute that will dissolve in a given amount of solvent under a given set of conditions. Many factors affect the numerical value of a solute's solubility in a given solvent, including the nature of the solvent itself, the temperature, and, in some cases, the pressure and presence of other solutes.

Most solids become more soluble in water with increasing temperature. As the pressure of a gas above a liquid increases, the solubility of the gas increases; conversely, as the pressure of the gas decreases, its solubility decreases.

A saturated solution is a solution that contains the maximum amount of solute that can be dissolved under the conditions at which the solution exists. A saturated solution containing excess undissolved solute is an equilibrium situation where an amount of undissolved solute is continuously dissolving while an equal amount of dissolved solute is continuously crystallizing.

Sometimes it is possible to exceed the maximum solubility of a compound, producing a ***supersaturated*** solution. ***A supersaturated solution*** is an unstable solution that temporarily contains more dissolved solute than that present in a saturated solution.

An unsaturated solution is a solution that contains less than the maximum amount of solute that can be dissolved under the conditions at which the solution exists. Most solutions are fall into this category.

The rate at which a solution forms is governed by how rapidly the solute particles are distributed throughout the solvent. Three factors that affect the rate of solution formation are:

1. *the surface area*, and thus fewer solvent molecules can interact with it at a given time.

2. *the degree of agitation during solution preparation.* Stirring solution components disperses the solute particles more rapidly, increasing the possibilities for solute- solvent interactions. Hence the rate of solution formation is increased.

3. *the temperature of the solution components*. Solution formation occurs more rapidly as the temperature is increased. At a higher temperature, both solute and solvent molecules move more rapidly so more interactions between them occur within a given time period.

Solution formation and solubility rules. In a solution, solute particles are uniformly dispersed throughout the solvent. Considering what happens at the molecular level during the solution process will help us understand how this is accomplished.

In order for a solute to dissolve in a solvent, two types of interparticle attractions must be overcome: (1) attractions between solute particles (solute-solute attractions) and (2) attractions between solvent particles (solvent-solvent attractions). Only when these attractions are overcome can particles in both pure solute and pure solvent separate from one another and begin to intermingle. A new type of interaction, which does not exist prior to solution formation, arises as a result of the mixing of solute and solvent. This new interaction is the attraction between solute and solvent particles (solute-solvent attractions). These attractions are the primary driving force for solution formation.

The random motion of solute ions in solutions causes them to collide with one another, with solvent molecules, and occasionally with the surface of any undissolved solute. Ions undergoing the latter type of collision occasionally stick to the solid surface and thus leave the solution. When the number of ions in solution is low, the chances for collision with the undissolved solute are low. However, as the number of ions in solution increases, so do the chances for collisions, and more ions are recaptured by the undissolved solute. Eventually, the number of ions in solution reaches a level where ions return to the undissolved solute at the same rate at which other ions leave.

Solubility rules are based on polarity considerations – specifically, on the magnitude of the difference between the polarity of the solute and solvent. In general, it is found that the greater the difference in solute-solvent polarity, the less soluble is the solute. This means that *substances of like polarity tend to be more soluble in each other than substances that differ in polarity.* This conclusion is often expressed as the simple phrase "*like dissolves like."* Polar substances, in general, are good solvents for other polar substances but not for nonpolar substances. Similarly, nonpolar substances exhibit greater solubility in nonpolar solvents than in polar solvents.

The generalization "like dissolves like" is a useful tool for predicting solubility behavior in many, but not all, solute-solvent situations. Results that agree with this generalization are nearly always obtained in the cases of gas-in-liquid and liquid-in-liquid solutions and for solid-in-liquid solutions in which the solute is not an ionic compound. For example, NH_3 gas (a polar gas) is much more soluble in H_2O (a polar liquid) than is O_2 gas (a nonpolar gas).

In the common case of solid-in-liquid solutions in which the solute is an ionic compound, the rule "like dissolves like" is not adequate. Their polar nature would suggest that all ionic compounds are soluble in a polar solvent such as water, but this is not the case. The failure of the generalization for ionic compounds is related to the complexity of the factors involved in determining the magnitude of the solute-solute (ion-ion) and solvent-solute (solvent-ion) interactions. Among other things, both the charge and the size of the ions in the solute must be considered. Changes in these factors affect both types of interactions, but not to the same extent.

5.2 Solution concentration units

Because solutions are mixtures, they have a variable composition. Specifying what the composition of a solution is involves specifying solute concentrations. ***A concentration*** is the amount of solute present in a specified amount of solution. Many methods of expressing concentration exist, and certain methods are better suited for some purposes than others.

Percent concentration. There are three different ways of representing percent concentration:

- Percent by mass (or mass-mass percent);
- Percent by volume (or volume-volume percent);
- Mass-volume percent.

Percent by mass (or mass-mass percent) is the percentage unit most often used in chemical laboratories. ***Percent by mass*** is the mass of solute in a solution divided by the total mass of solution, multiplied by 100 (to put the value in terms of percentage).

$$\text{percent by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \cdot 100\%$$

Mass of solution = mass of solute + mass of solvent

The second type of percentage unit, percent by volume (or volume-volume percent), which is abbreviated % (v/v), is used as a concentration unit in situations where the solute and solvent are both liquids or both gases. In these cases, it is more convenient to measure volumes than masses. ***Percent by volume*** is the volume of solute in a solution divided by the total volume of solution, multiplied by 100.

$$\text{percent by volume} = \frac{\text{volume of solute}}{\text{total volume of s olution}} \cdot 100\%$$

Solute and solution volumes must always be expressed in the same units when you use percent by volume.

The third type of percentage unit in common use is mass-volume percent; it is abbreviated % (m/v). This unit, which is often encountered in clinical and hospital settings, is particularly convenient to use when you work with a solid solute, which is easily weighed, and a liquid solvent. Solutions of drugs for internal and external use, intravenous and intramuscular injectables, and reagent solutions for testing are usually labeled in mass-volume percent.

Mass-volume percent is the mass of solute in a solution (in grams) divided by the total volume of solution (in milliliters), multiplied by 100. ***Molarity*** is the moles of solute in a solution divided by the liters of solution.

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solvent}} \cdot 100\%$$

Note that the abbreviation for molarity is a capital M. A solution containing 1 mole of KBr in 1 liter of solution has a molarity of 1 and is said to be a 1 M (1 molar*)* solution.

The molarity concentration unit is often used in laboratories where chemical reactions are being studied. Because chemical reactions occur between molecules and atoms, use of the mole a unit that counts particles – is desirable. Equal volumes of two solutions of the same molarity contain the same number of solute molecules.

Mole fraction (X) is the number of moles of component A divided by the total number of moles of all components.

$$\text{mole fraction of A} = \frac{\text{moles of A}}{\text{moles of all components}} \cdot 100\%$$

Molality (m) is the number of moles of solute dissolved in 1 kg of solvent

$$\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent}}$$

5.3 Acids and bases. Ionic equilibrium

Arrhenius concept. An acid is any species that increases the concentration of hydronium ions (H_3O^+), in aqueous solution. A base is any species that increases the concentration of hydroxide ion, (OH^-), in aqueous solution.

For an acid: $HCl + H_2O = H_3O^+ + Cl^-$

For a base: $NH_3 + H_2O = NH_4^+ + OH^-$

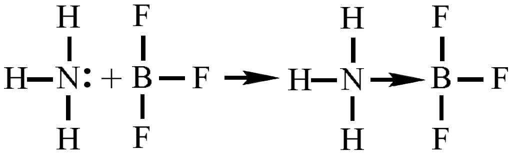
However, the drawback with the Arrhenius concept is that it only applies to aqueous solutions.

Bronsted-lowery concept. An acid is a species which can donate a proton (i.e., a hydrogen ion, H^+) to a proton acceptor. A base is a species which can accept a proton from a proton donor. Along with the Bronsted-lowery concept of a proton donor (acid) and a proton acceptor (base), arises the concept of conjugate acid-base pairs.

For example, when the acid HCl reacts, it donates a proton thereby leaving Cl^- (which is now a proton acceptor or the conjugate base of HCl). Using NH_3 as the base and H_2O as the acid:

$$\underset{\substack{\uparrow\\ \text{base}}}{NH_3} + \overset{\substack{\text{acid}\\ \downarrow}}{H_2O} = \underset{\substack{\uparrow\\ \text{conjugate acid}}}{NH_4^+} + \overset{\substack{\text{conjugate base}\\ \downarrow}}{OH^-}$$

Lewis concept. An acid is a species that can accept a pair of electrons. A base is a species that can donate a pair of electrons.



$$H-\underset{\displaystyle H}{\overset{\displaystyle H}{N}}: + \underset{\displaystyle F}{\overset{\displaystyle F}{B}}-F \longrightarrow H-\underset{\displaystyle H}{\overset{\displaystyle H}{N}}\rightarrow\underset{\displaystyle F}{\overset{\displaystyle F}{B}}-F$$

Equilibrium of water. The reaction of autoionization of water is:

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^- \qquad (4.14)$$

The equilibrium expression is:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]} \qquad (4.15)$$

Since the concentration of water is a constant (55.55 M), $[H_2O]^2$ can be included in the equilibrium constant, K. this new constant is now called K_w:

$$K_w = K[H_2O]^2 = [H_3O^+][OH^-]$$

$\boldsymbol{K_w}$ is the ion product constant for water, also called the ionization constant or dissociation constant for water. The ionization constant for water at 25 °C has a value of $\mathbf{1.0 \cdot 10^{-14}}$. The equilibrium expression now becomes:

$$K_w = 10^{-14} = [H_3O^+][OH^-] \qquad (4.16)$$

When the concentration of hydrogen ions equals the concentration of hydroxide ions the solution is said to be neutral.

pH is the measure of how strong or weak an acid is, and is defined as the negative of the log of the hydrogen ion concentration, or:

$$\mathrm{pH} = -\lg[H_3O^+] \qquad (4.17)$$

Water has a pH of 7, this is calculated from the dissociation constant for water:

$$[H_3O^+] = 10^{-7};\ \mathrm{pH} = -\lg[H_3O^+];\ \mathrm{pH} = 7$$

The concept of pH can be applied to any system in which hydrogen ions are produced. An acidic solution would have an excess of hydrogen ions, a basic solution would have an excess of hydroxide ions, and a neutral solution the hydrogen ions would equal the hydroxide ions. Since pH is a measure of the hydrogen ion concentration, acidic and basic solutions can be distinguished on the basis of their pH.

- acidic solutions: $[H_3O^+] > 10^{-7}$ M, $pH < 7$;
- basic solutions: $[H_3O^+] < 10^{-7}$ M, $pH > 7$;
- neutral solutions: $[H_3O^+] = 10^{-7}$ M, $pH = 7$.

For a monoprotic acid HA, the equilibrioum reaction is:

$$HA_{(aq)} + H_2O \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}.$$

And the equilibrium expression is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The equilibrium constant, ***K_a*** is called the acid dissociation constant. Similarly for a polyprotic acid (i.e. phosphoric acid), the equilibrium reactions are:

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \qquad K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \qquad K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-} \qquad K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

For a base, the equilibrium reaction is:

$$B + H_2O \leftrightarrow BH^+ + OH^-.$$

And the equilibrium expression is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The equilibrium constant, $\boldsymbol{K_b}$ is called the base dissociation constant. Relationship between K_a and K_b conjugate pair:

$$K_aK_b = [H_3O^+][OH^-] = 10^{-14}$$
$$pK_a + pK_b = 14$$

5.4 Hydrolysis

Hydrolysis is the between water and the ions of a salt.

- Salt of a strong acid – strong base.

Consider NaCl, the salt of a strong acid and a strong base. The hydrolysis of this salt would yield NaOH and HCl. Since both species would completely dissociate into their respective ions yielding equivalent amounts of H_3O^+ and OH^-, the overall net effect would be that no hydrolysis takes place. Since $[H_3O^+] = [OH^-]$, the pH would be 7, a neutral solution.

- Salt of a strong acid – weak base.

Consider the hydrolysis of NH_4Cl:

$$NH_4{}^+ + H_2O \square\ H_3O^+ + NH_3$$

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

$$K_h = \frac{K_w}{K_b}$$

$$K_h = \frac{[\mathrm{H_3O^+}][\mathrm{OH^-}]}{[\mathrm{NH_4^+}][\mathrm{OH^-}]/[\mathrm{NH_3}]} = \frac{[\mathrm{H_3O^+}][\mathrm{NH_3}]}{[\mathrm{NH_4^+}]}$$

- Salt of a weak acid – strong base.

Consider the hydrolysis of $NaC_2H_3O_2$:

$$C2H_3O_2^- + H_2O \leftrightarrow HC_2H_3O_2 + OH^-,$$

$$K_h = \frac{[\mathrm{HC_2H_3O_2}][\mathrm{OH^-}]}{[\mathrm{C_2H_3O_2^-}]}$$

$$K_h = \frac{K_w}{K_b} = \frac{[\mathrm{H_3O^+}][\mathrm{OH^-}]}{[\mathrm{H_3O^+}][\mathrm{C_2H_3O_2^-}]/[\mathrm{HC_2H_3O_2}]} = \frac{[\mathrm{HC_2H_3O_2}][\mathrm{OH^-}]}{[\mathrm{C_2H_3O_2^-}]}$$

- Solubility product

In the case for which a solid is being dissolved, the general chemical reaction becomes:

$$A_aB_b \leftrightarrow aA + bB$$

and the equilibrium expression is:

$$K = \frac{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}{[\mathrm{A_aB_b}]}$$

the denominator in the expression $[A_aB_b]$ represents the concentration of the pure solid and is constant, therefore it can be incorporated into the equilibrium constant *K*. The expression now becomes:

$$K_{sp} = [\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}$$

For example, a saturated solution of AgCl, would have the following equilibrium:

$$AgCl(s) \leftrightarrow Ag^+ + Cl^-.$$

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

The value of the K_{sp} for AgCl is $1.7 \cdot 10^{-10}$

$$1.7 \cdot 10^{-10} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

If the ion product is equal to or less that the K_{sp} no precipitate will form. If the ion product is greater than the K_{sp} value, the material will precipitate out of solution so that the ion product will be equal to the K_{sp}.

5.5 Common ion effect

The common ion is when an ion common to one of the salt ions is introduced to the solution. The introduction of a common ion produces an effect on the equilibrium of the solution and according to ***Lc Chatclicr's principle***, i.e. the equilibrium is shifted so as to reduce the effect of the added ion. This is referred to as the common ion effect.

In the case of a solution of AgCl, if NaCl is added, the common ion being Cl^- the equilibrium would be shifted to the left so that the ion product will preserve the value of the K_{sp}.

CONCEPTS TO REMEMBER

Solution components. The component of a solution that is present in the greatest amount is the *solvent.* A *solute* is a solution component that is present in a small amount relative to the solvent.

Solution characteristics. A solution is a homogeneous (uniform) mixture. Its composition and properties are dependent on the ratio of solute(s) to solvent. Dissolved solutes are present as individual particles (molecules, atoms, or ions).

Solubility. The solubility of a solute is the maximum amount of solute that will dissolve in a given amount of solvent. The extent to which a solute dissolves in a solvent depends on the structure of solute and solvent, the temperature, and the pressure. Molecular polarity is a particularly important factor in determining solubility. A *saturated* solution contains the maximum amount of solute that can be dissolved under the conditions at which the solution exists.

Solution concentration. Solution concentration is the amount of solute present in a specified amount of solution. Percent solute and molarity are commonly encountered concentration units. Percent concentration units include percent by mass, percent by volume, and mass-volume percent. Molarity gives the moles of solute per liter of solution.

Dilution. Dilution involves adding solvent to an existing solution. Although the amount of solvent increases, the amount of solute remains the same. The net effect of dilution is a decrease in the concentration of the solution.

SAMPLE PROBLEMS WITH SOLUTIONS

Problem 1

Write the complete ionic and net ionic equations for each of the following reaction:

$$2\,Na_3PO_{4(aq)} + 3CaCl_{2(aq)} \rightarrow 6\,NaCl_{(aq)} + Ca_3(PO_4)_{2(s)}$$

Solution

When aqueous solutions of sodium phosphate and calcium chloride are mixed together, an insoluble white solid forms. This precipitation reaction is described by the following equation:

$$2\,Na_3PO_{4(aq)} + 3CaCl_{2(aq)} \rightarrow 6\,NaCl_{(aq)} + Ca_3(PO_4)_{2(s)}$$

An equation such as this one is commonly called a molecular equation. A molecular equation is one that shows the chemical formulas of all reactants and products but does not expressly indicate their ionic nature. The complete ionic equation is used to describe the chemical reaction while also clearly indicating which of the reactants and/or products exist primarily as ions in aqueous solution.

To write the complete ionic equation:

1. Start with a <u>balanced</u> molecular equation.

2. Break all soluble strong electrolytes (compounds with (aq) beside them) into their ions:

- indicate the correct formula and charge of each ion;
- indicate the correct number of each ion;
- write (aq) after each ion.

3. Bring down all compounds with (s), (l), or (g) unchanged.

For the reaction given above, the complete ionic equation is:

$$6\,Na^+_{(aq)} + 2PO^{3-}_{4(aq)} + 3Ca^{2+}_{(aq)} + 6Cl^-_{(aq)} \rightarrow 6\,Na^+_{(aq)} + 6Cl^-_{(aq)} + Ca_3(PO_4)_{2(s)}$$

How did I get this equation? Consider each reactant or product separately:

1. 1 mole of Na_3PO_4 contains 3 moles of Na^+ and 1 mole of PO_4^{3-}. Since the balanced equation shows that two moles of sodium phosphate are involved in the reaction, a total of 6 moles

(2·3) of Na^+ and 2 moles (2·1) of PO_4^{3-} are formed. Notice that the subscript "4" in the formula for the phosphate ion is not used when determining the number of phosphate ions present. That particular subscript is part of the formula for the phosphate ion itself.

$$2\,Na_3PO_{4(aq)} \rightarrow 6\,Na^+{}_{(aq)} + 2\,PO_4^{3-}{}_{(aq)}$$

2. 1 mole of $CaCl_2$ contains 1 mole of Ca^{2+} and 2 moles of Cl^-. Remember, the subscript "2" indicates the number of chloride ions. Cl_2 is elemental chlorine. You will never have a diatomic chlorine ION (i.e. Cl_2^- or Cl_2^{2-}) in aqueous solution. Since the balanced equation shows that 3 moles of calcium chloride are involved in the reaction a total of 3 moles (3·1) of Ca^{2+} and 6 moles (3·2) of Cl^- are formed.

$$3CaCl_{2(aq)} \rightarrow 3Ca^+{}_{(aq)} + 6\,Cl^-{}_{(aq)}$$

3. 1 mole of NaCl contains 1 mole of Na^+ and 1 mole of Cl^-. Since the balanced equation shows that 6 moles of NaCl are produced by the reaction, 6 moles (6·1) of Na^+ and 6 moles (6·1)of Cl^- will be formed.

$$6\,NaCl_{(aq)} \rightarrow 6\,Na^+{}_{(aq)} + 6\,Cl^-{}_{(aq)}$$

4. Since calcium phosphate is an insoluble solid (indicated by the (s) beside its formula), it will not form appreciable amounts of ions in water. It is brought down unchanged into the complete ionic equation.

5. Writing Net Ionic Equations:

In the previous example, the complete ionic equation for the reaction between sodium phosphate and calcium chloride was:

$$6\,Na^+_{(aq)} + 2\,PO^{3-}_{4(aq)} + 3Ca^{2+}_{(aq)} + 6Cl^-_{(aq)} \rightarrow 6\,Na^+_{(aq)} + 6Cl^-_{(aq)} + Ca_3(PO_4)_{2(s)}$$

If you look at the ions present on the reactant and product sides of the equation, you will notice that some of the ions are exactly the same. For example, 6 Na^+ (aq) are present on both sides of the equation. Also, 6 Cl^- (aq) are present on both sides of the equation. That means that the sodium ions and the chloride ions were present in the reaction mixture but DID NOT PARTICIPATE in the reaction. The sodium and chloride ions in this reaction are referred to as spectator ions.

Spectator ions are ions that are present in the reaction mixture but do not participate in it. They "sit around and watch the reaction take place" just like a spectator at a basketball game watches the players in the game but doesn't play the game himself. You can recognize spectator ions by looking for ions that are present on both sides of the equation. They will always have the same exact formula, charge, and physical state. They will also be present in exactly the same number on both sides of the equation.

To write a net ionic equation:

- write the balanced molecular equation.
- write the balanced complete ionic equation.
- cross out the spectator ions that are present.
- write the "leftovers" as the net ionic equation.

For the example reaction that we have been considering, the net ionic equation is found by crossing out the spectator ions from the complete ionic equation:

$$\cancel{6\,Na^{+}_{(aq)}} + 2\,PO^{3-}_{4(aq)} + 3\,Ca^{2+}_{(aq)} + \cancel{6\,Cl^{-}_{(aq)}} \rightarrow \cancel{6\,Na^{+}_{(aq)}} + \cancel{6\,Cl^{-}_{(aq)}} + Ca_3(PO_4)_{2(s)}$$

and then re-writing the "leftovers:"

$$2\,PO^{3-}_{4(aq)} + 3\,Ca^{2+}_{(aq)} \rightarrow Ca_3(PO_4)_{2(s)}$$

Problem 2

Write the equation and the equilibrium expression for the dissolving of barium sulfate.

Solution

$$BaSO_{4(s)} \rightarrow Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

Make an "ICE" chart.

Let "x" represent the barium sulfate that dissolves in the sodium sulfate solution expressed in moles per liter.

	$BaSO_{4\,(s)}$	$Ba^{2+}\ _{(s)}$	$SO_4^{\ 2-}\ _{(aq)}$
Initial concentration	All solid	0	0.020 M (from Na_2SO_4)
Change in concentration	– x dissolves	+ x	+ x
Equilibrium concentration	Less solid	x	0.020 M + x

Substitute into the equilibrium expression and solve for x. We will make the assumption that since x is going to be very small (the solubility is reduced in the presence of a common ion), the term "0.020 + x" is the same as "0.020." (You can leave x in the term and use the quadratic equation or the method of successive approximations to solve for x, but it will not improve the significance of your answer.)

$$1.1 \cdot 10^{-10} = [x][0.020 + x] = [x][0.020]$$
$$x = 5.5 \cdot 10^{-9}\ M$$

INDIVIDUAL TEST PAPER

Exercise 1

Write the ionic and molecular equations of possible chemical reaction between the substances presented in table 5.1.

Table 5.1 – Variants of the problem

Variant	Substances		
1	H_2SO_4	Na_2S	$NaOH$
2	$NiCl_2$	H_2SO_3	$Ba(OH)_2$
3	K_2CO_3	$CdSO_4$	$RbOH$
4	$Al(NO_3)_3$	K_3PO_4	$Ba(OH)_2$
5	$Mn(CH_3COO)_2$	$(NH_4)_2SO_3$	KOH
6	$BaCl_2$	$LiOH$	H_2SO_4
7	$Pb(NO_3)_2$	$(NH_4)_2S$	KOH
8	$Co(NO_3)_2$	$Sr(OH)_2$	H_2SO_4
9	$MgSO_4$	SnF_2	KOH
10	$CuSO_4$	KOH	$(NH_4)_2SO_3$
11	$CuCl_2$	HF	MgS
12	$FeCl_2$	$LiOH$	H_2CO_3
13	HCl	Na_2S	$Ba(OH)_2$
14	$Ca(OH)_2$	K_2CrO_4	HNO_3
15	HCl	$Pb(CH_3COO)_2$	K_2S
16	$ZnSO_4$	$NaOH$	K_3PO_4
17	$Ba(OH)_2$	H_2SO_3	$CaCl_2$
18	$Fe(NO_3)_3$	MgS	H_2SO_4
19	$CrCl_3$	Na_2SiO_3	H_3PO_4
20	$NaOH$	NH_4Cl	H_2SO_4
21	$NaOH$	$NiSO_4$	H_2SO_3

Continued of table 5.1

Variant	Substances		
22	$SnBr_2$	$AgNO_3$	LiOH
23	Pb $(CH_3COO)_2$	KOH	HNO_3
24	$Ba(OH)_2$	$(NH_4)_2S$	$CoCl_2$
25	$HgSO_3$	$BaCl_2$	H_2SO_4

Exercise 2

Calculate the equilibrium concentrations of ions in saturated solution of the compound (table 5.2), using the soluble production values (application B).

Table 5.2 – Variants of the problem

Variant	Substance	Variant	Substance	Variant	Substance
1	AgBr	10	Bi_2S_3	19	$Al(OH)_3$
2	$Be(OH)_2$	11	CaF_2	20	Ag_3PO_4
3	$PbBr_2$	12	$AlPO_4$	21	$Ca(OH)_2$
4	Sb_2S_3	13	$Sc(OH)_3$	22	SrF_2
5	$Mg(OH)_2$	14	AgI	23	$Zn(OH)_2$
6	$AuCl_3$	15	PbI_2	24	$BaSO_4$
7	$Cd(CN)_2$	16	$BaCO_3$	25	Tl_2S
8	$PtBr_4$	17	Tl_2CO_3	26	Li_3PO_4
9	AgCN	18	$Cd(OH)_2$	27	$Fe(OH)_2$

Exercise 3

Write the first step dissociation reaction of a substance (table 5.3). Determine, using application C and D:

- dissociation degree α**;**

- concentration of ions H^+ or OH^-;
- pH of solution.

Table 5.3 – Variants of the problem

Variant	Electrolyte	Concentration, mol/l	Variant	Electrolyte	Concentration, mol/l
1	HNO_2	0,02	14	H_3PO_3	0,05
2	H_3BO_3	1,50	15	H_2TeO_3	0,65
3	$HBrO$	0,25	16	HNO_2	1,50
4	HCN	2,80	17	H_2Te	0,56
5	H_2SiO_3	0,03	18	HIO	0,01
6	H_3AsO_3	1,75	19	H_2CO_3	0,75
7	$HCOOH$	0,10	20	H_2SiO_3	1,00
8	H_2SeO_3	0,03	21	CH_3COOH	0,90
9	HIO	1,55	22	$HClO$	0,75
10	H_2Se	2,10	23	H_3PO_4	1,80
11	H_2SO_3	1,45	24	HF	1,00
12	$HClO_2$	1,65,	25	H_3AsO_4	0,10
13	H_2S	0,20	26	H_2SO_3	0,50

Exercise 4

Write the first step ionic and molecular reaction of a salt (table 5.4) hydrolysis.

Table 5.4 – Variants of the problem

Variant	Salt	Variant	Salt	Variant	Salt
1	Li_2CO_3 $CuCl_2$	2	Na_3PO_4 $NiSO_4$	3	Li_2S $Cr(NO_3)_3$

Continued of table 5.4

Variant	Salt	Variant	Salt	Variant	Salt
4	$FeCl_3$ CH_3COOK	11	$Pb(NO_3)_2$ $HCOONa$	18	$ZnSO_4$ CH_3COONa
5	Na_2SO_3 $Co(NO_3)_2$	12	$Sc(ClO_4)_3$ KCN	19	K_2CO_3 $CoCl_2$
6	K_2SiO_3 $ZnCl_2$	13	Na_2SiO_3 $MgCl_2$	20	Li_2SO_3 $Al(NO_3)_3$
7	BaS $Al_2(SO_4)_3$	14	Cs_2CO_3 $BeSO_4$	21	Na_2S $Cd(ClO_4)_2$
8	$Cd(NO_3)_2$ K_2CO_3	15	Li_2Se $Cu(NO_3)_2$	22	$SnSO_4$ BaF_2
9	KF $MnCl_2$	16	KNO_2 $NiCl_2$	23	Cs_3PO_4 $MnCl_2$
10	Rb_3PO_4 $FeSO_4$	17	Rb_2S $Cr_2(SO_4)_3$	24	$CoSO_4$ $AgCl$

CHAPTER 6

Electrochemical processes and systems

6.1 The main provisions

By the nature of conduction and values of conductivity, materials can be classified as conductors, semiconductors, or insulators (dielectrics). It is a special attribute of conductors that free electric charges are present in them. The migration of these free charges in an applied electric field manifests itself as electric current.

Conduction of electric current in conductors can be electronic or ionic, depending on the type of charge involved. Substances exist where conduction is mixed (i.e., where both ions and electrons are moving). Electronic conduction is found in all metals and also in certain other substances: carbon materials (graphite, carbon black), some oxides and other inorganic compounds (e.g., tungsten carbide), and number of organic substances. Ionic conductors (conductors of the second kind) are also known as electrolytes.

The main topic of electrochemistry is investigation of the properties of ionic conductors and of electric circuits containing ionic conductors, and investigation of phenomena occurring during passage of an electric current through such circuits. Aqueous solutions of acids, bases, and salts are the ionic conductors used most widely and studied most thoroughly.

6.2 Potential differences at interfaces

The transition region between two phases consists of a region of charge unbalance known as the electric double layer. As its name implies, this consists of an inner monomolecular layer of adsorbed water molecules and ions, and an outer diffuse region that compensates for any local charge unbalance that gradually merges into the completely random arrangement of the bulk solution. In the case of a metal immersed in pure water, the electron fluid within the metal causes the polar water molecules to adsorb to the surface and orient them selves so as to create two thin planes of positive and negative charge. If the water contains dissolved ions, some of the larger (and more polarizable) anions will loosely bond (chemi-sorb) to the metal, creating a negative inner layer which is compensated by an excess of cations in the outer layer.

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte (Fig. 6.1). A process of this kind can always be represented as a chemical reaction and is known generally as an electrode process. Electrode processes take place within the double layer and produce a slight unbalance in the electric charges of the electrode and the solution. Much of the importance of electrochemistry lies in the ways that these potential differences can be related to the thermodynamics and kinetics of electrode reactions. In particular, manipulation of the interfacial potential difference affords an important way of exerting external control on an electrode reaction.

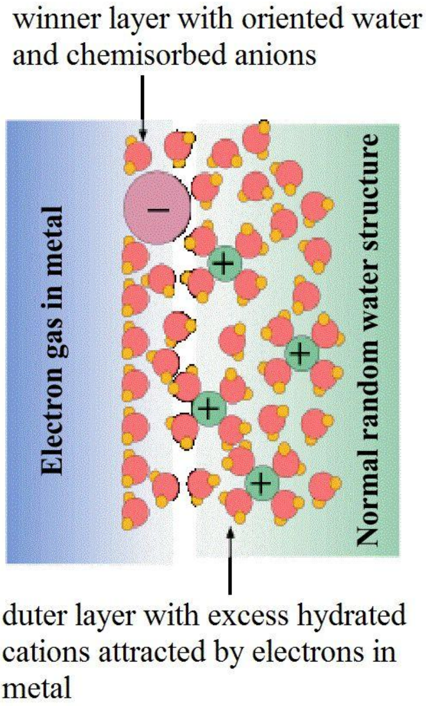
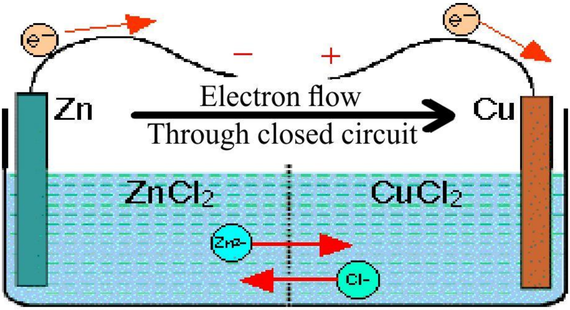


Figure 6.1 – Electric double layer at an electrode surface

The interfacial potential differences which develop in electrode-solution systems are limited to only a few volts at most. This may not seem like very much until you consider that this potential difference spans a very small distance. In the case of an electrode immersed in a solution, this distance corresponds to the thin layer of water molecules and ions that attach themselves to the electrode surface – normally only a few atomic diameters. Thus a very small voltage can produce a very large potential gradient. For example, a potential difference of one volt across a typical 10^{-8} cm interfacial boundary amounts to a potential gradient of 100 million volts per centimeter – a very significant value.

6.3 Electrochemical cells

Although it is physically impossible to measure or manipulate the potential difference between a piece of metal and the solution in which it is immersed, we can easily measure a potential difference between two such electrodes immersed in a solution (Fig. 6.2). The result will be the sum of the two electrode potentials, we shall see farther on that such measurements can be supply all the information we need in order to characterize the two electrode reactions.



$$Zn^{o} - 2\bar{e} \rightarrow Zn^{2+} \qquad Cu^{2+} + 2\bar{e} \rightarrow Cu^{o}$$

Figure 6.2 – A simple electrochemical cell

The two compartments of this cell are separated by a porous barrier that allows ions to pass through while preventing gross mixing of the two solutions. When the two electrodes are connected, charges flow in the directions indicated. Note thatthe buildup of positive charge on the left side can be offset either by diffusion of Zn^{2+} to the right or (less efficiently) by Cl^{-} to the left. This arrangementis called a galvaniccell. A typical cell might consist of two pieces of metal, one zinc and the other copper, each immersed each in a solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapid limiting but allows ions to diffuse through.

If we simply left it at that, no significant amount of reaction would take place. However, if we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions go into solution in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the same as before – the oxidation of zinc by copper (II) ions:

$$\mathrm{Zn^o + Cu^{2+} \rightarrow Zn^{2+} + Cu^o}$$

but this time, the oxidation and reduction steps take place in separate locations:

left electrode:	$\mathrm{Zn^o - 2\overline{e} \rightarrow Zn^{2+}}$	oxidation
right electrode:	$\mathrm{Cu^{2+} + 2\overline{e} \rightarrow Cu^o}$	reduction

Electrochemical cells allow measurement and control of a redox reaction. The reaction can be started and stopped by connecting or disconnecting the two electrodes. If we place a variable resistance in the circuit, we can even control the rate of the net cell reaction by simply turning a knob. By connecting a battery or other source of current to the two electrodes, we can force the reaction to proceed in its non-spontaneous, or reverse direction.

By placing an ammeter in the external circuit, we can measure the amount of electric charge that passes through the electrodes, and thus the number of moles of reactants that get transformed into products in the cell reaction.

Electric charge q is measured in coulombs. The amount of charge carried by one mole of electrons is known as the faraday, which we denote by F. Careful experiments have determined that ***1F*** ≈ 96467 C/mol. For most purposes, you can simply use ***96,500 C/mol*** as the value of the faraday.

When we measure electric current, we are measuring the rate at which electric charge is transported through the circuit. A current of one ampere corresponds to the flow of one coulomb per second.

Cell description conventions. In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the cell of Fig. 6.2 would be:

$$(-)\,\mathrm{Zn}_{(s)}\left|\mathrm{Zn}^{2+}_{(aq)}\right\|\mathrm{Cu}^{2+}_{(aq)}\left|\mathrm{Cu}_{(s)}\right.(+)$$

In this notation, the vertical bars indicate phase boundaries; the double vertical bar in the middle denotes the phase boundary between the two solutions. As a matter of convention, the chemical species that undergo reduction when the cell reaction proceeds to the right according to the net equation are shown on the right side, and those that undergo oxidation are shown on the left. Note carefully that this is entirely independent of the physical location of the two electrodes in the actual cell in Fig. 6.2.

There are several other conventions relating to cell notation and nomenclature that you are expected to know:

1. The anode is where oxidation occurs, and the cathode is the site of reduction. In an actual cell, either electrode can have either identity, depending on the direction in which the net cell reaction is occurring.

2. If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) when the cell operates iz its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be positive.

"Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

6.4 Electrodes and electrode reactions

The electron-transfer step that takes place at each electrode is known as the electrode reaction. The substances that receive and lose electrons are called theelectroactive species (Fig. 6.3).

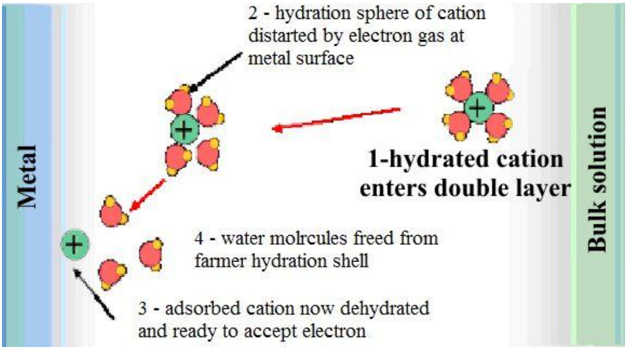


Figure 6.3 – Electron transfer at an electrode

This process takes place within the very thin interfacial region at the electrode surface, and involves quantum-mechanical tunneling of electrons between the electrode and the electroactive species. The work required to displace the H_2O molecules in the hydration spheres of the ions constitutes part of the activation energy of the process.

In the example of the Zn/Cu cell we have been using, the electrode reaction involves a metal and its hydrated cation; we call such electrodes metal-metal ion electrodes. There are a number of other kinds of electrodes which are widely encountered in electrochemistry and analytical chemistry.

The Nernst equation. The standard cell potentials we have been discussing refer to cells in which all dissolved substances are at unit activity, which essentially means an "effective concentration" of 1M. Similarly, any gases that take part in an electrode reaction are at an effective pressure (known as the fugacity) of 1 atm. If these concentrations or pressures have other values, the cell potential will change in a manner that can be predicted from the principles you already know.

Suppose, for example, that we reduce the concentration of Zn^{2+} in the Zn/Cu cell from its standard effective value of 1M to an to a much smaller value:

$$(-)\,Zn_{(s)}\left|Zn^{2+}_{(aq)}(0.01M)\right\|Cu^{2+}_{(aq)}\left|Cu_{(s)}(+)\right.$$

This will reduce the value of Q for the cell reaction:

$$Zn^{o} + Cu^{2+} \rightarrow Zn^{2+} + Cu^{o}$$

thus making it more spontaneous, or "driving it to the right" as the ***Le Chatelier principle*** would predict, and making its free energy change ΔG more negative than $\Delta G°$, so that E would be more positive than $E°$.

The relation between the actual cell potential E and the standard potential $E°$ is developed in the following way. We begin with equation 6.1, which relates the standard free energy change (for the complete conversion of products into reactants) to the standard potential:

$$\Delta G^{\circ} = -nFE^{\circ} \qquad (6.1)$$

By analogy we can write the more general equation:

$$\Delta G = -nFE \qquad (6.2)$$

which expresses the change in free energy for any extent of reaction – that is, for any value of the reaction quotient Q. We now substitute these into the expression that relates G and $G°$ which you will recall from the chapter on chemical equilibrium:

$$\Delta G = \Delta G^{\circ} + RT\ln Q$$

which gives:

$$-nFE = -nFE^{\circ} + RT\ln Q$$

which can be rearranged to:

$$E = E^{\circ} - \frac{RT}{nF}\ln Q \qquad (6.3)$$

The Nernst equation is more commonly written in base – 10 log form and for 25°C:

$$E_{\mathrm{M}^{z+}/\mathrm{M}} = E^{\circ}_{\mathrm{M}^{z+}/\mathrm{M}} + \frac{0.059}{z}\lg c(\mathrm{M}^{z+}) \qquad (6.4)$$

Electolytic cells. Electrolysis refers to the decomposition of a substance by an electric current. The electrolysis of sodium and potassium hydroxides, first carried out in 1808 by Sir Humphrey Davey, led to the discovery of these two metallic elements and showed that these two hydroxides which had previously been considered un-decomposable and thus elements were in fact compounds:

Electrolysis of molten alkali halides is the usual industrial method of preparing the alkali metals:

cathode reaction: $Na^+ + \bar{e} \rightarrow Na(l)$ $E^0 = -2.77$ V

anode reaction: $Cl^- - \bar{e} \rightarrow 0.5Cl_2(g)$ $E^0 = +1.36$ V

net reaction: $Na^+ + Cl^- \rightarrow Na(l) + 0.5Cl_2(g)$

Ions of alkali and alkali-earth metals in aqueous solutions can’t be reduced. Thus if a solution of sodium chloride undergoes electrolysis at platinum electrodes, the reactions are:

cathode reaction: $2H_2O + 2\bar{e} \rightarrow 2OH^- + H_2(g)$ $E^0 = -0.42$ V

$([OH^-] = 10^{-7}M)$

anode reaction : $Cl^- - \bar{e} \rightarrow 0.5Cl_2(g)$ $E^0 = +1.36$ V

net reaction: $2H_2O + Cl^- \rightarrow 2OH^- + H_2(g) + 0.5Cl_2(g)$

Both of these processes are carried out in electrochemical cells which are forced to operate in the "reverse", or non-spontaneous direction, as indicated by the negative for the above cell reaction. The free energy is supplied in the form of electrical work done on the system by the outside world (the surroundings). This is the only fundamental difference between an electrolytic cell and the galvanic cell in which the free energy supplied by the cell reaction is extracted as work done on the surroundings.

A common misconception about electrolysis is that "ions are attracted to the oppositely-charged electrode". This is true only in the very thin interfacial region near the electrode surface. Ionic motion throughout the bulk of the solution is by diffusion, which is transport of molecules in response to a concentration gradient (Fig 6.4).

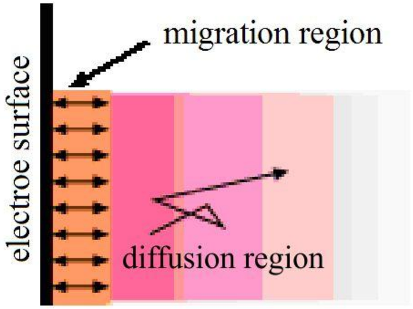


Figure 6.4 – Diffusion and migration in an electrolytic cell

Migration – the motion of a charged particle due to an applied electric field is only a minor player, producing only about one non-random jump out of around 100.000 random ones for a 1 V/cm electric field. Only those ions that find themselves within the interfacial region are likely to undergo migration.

6.5 Electrolysis in aqueous solutions

Water is capable of undergoing both oxidation:

$$2H_2O - 4\bar{e} \rightarrow 4H^+ + O_2(g) \qquad E^0 = +0.82\ \text{V}$$

and reduction:

$$2H_2O + 2\bar{e} \rightarrow 2OH^- + H_2(g) \qquad E^0 = -0.42\ \text{V}$$

Thus if an aqueous solution is subjected to electrolysis, one or both of the above reactions may be able to compete with the electrolysis of the solute.

This does not happen for the solution of NaCl illustrated above, but if we substitute sodium chloride for nickel chloride, metalic nickel is produced at the cathode instead of sodium and the side reaction is the hydrogen evolution:

cathode reaction: $Ni + 2e \rightarrow Ni^0$ $E^0 = -0.25$ V

$2H_2O + 2\bar{e} \rightarrow 2OH^- + H_2(g)$ $E^0 = -0.42$ V

In such case we use an active anode at wich undergoes
anode reaction : $Ni - 2e \rightarrow Ni^{2+}$.

The reason metallic sodium is not a product of this reaction is best understood by locating the couples Na/Na^+ and $H_2O/H_2, OH^-$. Reduction of Na^+ ($E^\circ = -2.7\,V$) is energetically more difficult than the reduction of water, so in aqueous solution the latter will prevail.

If we replace the chloride ion in the NaCl reaction with an anion such as nitrate or sulfate that is energetically much more difficult to oxidize, the water is oxidized instead. Electrolysis of a solution of sulfuric acid or of a salt such as $NaNO_3$ results in the decomposition of water at both electrodes:

cathode reaction: $2H_2O + 2\bar{e} \rightarrow 2OH^- + H_2(g)$

anode reaction: $2H_2O - 4\bar{e} \rightarrow 4H^+ + O_2(g)$

net reaction: $2H_2O \rightarrow 2H_2(g) + O_2(g)$

6.6 Faraday's laws of electrolysis

One mole of electric charge (96.500 C/mol), when passed through a cell, will discharge half a mole of a divalent metal ion such as Cu^{2+}. This relation was first formulated by Faraday in 1832 in the form of two laws of electrolysis:

1. The weights of substances formed at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.
2. The weights of different substances formed by the passage of the same quantity of electricity are proportional to the equivalent weight of each substance.

The equivalent weight of a substance is defined as the molar mass, divided by the number of electrons required to oxidize or reduce each unit of the substance. Thus one mole of V^{3+} corresponds to three equivalents of this species, and will require three faradays of charge to deposit it as metallic vanadium.

Most stoichiometric problems involving electrolysis can be solved without explicit use of Faraday's laws. The "chemistry" in these problems is usually very elementary; the major difficulties usually stem from unfamiliarity with the basic electrical units:

- current (amperes) is the rate of charge transport; 1 A = 1 C/s.
- power (watts) is the rate of energy production or consumption; 1 W = 1 J/s = 1 V·A; 1 W·s = 1 J, 1 kW·h = 3600 J.

CONCEPTS TO REMEMBER

Electrochemistry is a science that deals with the relation of electricity to chemical change sand with the inter conversion of chemical and electrical energy

Cathode is the electrode of an electrochemical cell at which reduction occurs:

- the negative terminal of an electrolytic cell
- the positive terminal of a galvanic cell

Anode is the electrode of an electrochemical cell at which oxidation occurs:

- the positive terminal of an electrolytic cell
- the negative terminal of a galvanic cell

Electrolysis is the process by which electric current is passed through a substance to effect a chemical change. The chemical change is one in which the substance loses orgains an electron (oxidation or reduction). The process is carried out in an electrolytic cell.

Electrolytic cell, any device in which electrical energy is converted to chemical energy, or vice versa. Such a cell typically consists of two metallic or electronic conductors (electrodes) held a part from each other and in contact with an electrolyte, usually a dissolved or fused ionic compound. Connection of the electrodes to a source of direct electric current renders one of them negatively charged and the other positively charged.

Electrical double layer, region of molecular dimension at the boundary of two substances across which an electrical field exists. The substances must each contain electrically charged particles, such as electrons, ions, or molecules with a separation of electrical charges (polar molecules). In the electrical double layer, oppositely charged particles attract each other and tend to collect at the surface of each substance but remain separated from one an other by the finite size of each particle or by neutral molecules that surround the charged particles. The electrostatic attraction between the two opposite and separated charges causes an electrical field to be established across the interface.

SAMPLE PROBLEMS WITH SOLUTIONS

Problem 1

In the cell of Fig. 6.2, how much mass would the zinc electrode lose if a current of 0.15 A flows through the external circuit for 1.5 hours?

Solution

The amount of charge passing between the electrodes is:
Q = 0.15A · 5400 s = 810 C or 810 C / 96500 C/mol = 0.0084 mol. Since the oxidation of one mole of Zn to Zn^{2+} results in the removal of two moles of electrons, the number of moles of Zn removed from the electrode is 0.0042 mol, corresponding to a weight loss of 0.043 mol · 65.37 g/mol = 0.275 g

Problem 2

The object to be plated with copper is placed in a solution of $CuSO_4$. What mass of copper will be deposited on the object if a current of 0.22 A flows through the cell for 1.5 hours?

Solution

Cu^{2+} ions are being reduced, the object acts as a cathode and must be connected to vie terminal (where the electrons come from) amount of charge passing through the cell is:

Q = 0.22 A · 5400 s = 1188 C;

1188 C / 96500 C/mol = 0.012 mol

reduction of one mole of Cu^{2+} ion requires the addition of two moles of electrons, ill discharge only 0.006 mol of Cu^{2+} whose mass will be 0.006 mol · 63.54 g/mol = 0.38 g of copper.

Problem 3

How much electric power is required to produce 1 metric ton (1000 kg) of chlorine from brine, assuming the cells operate at 2.0 V and assuming 100 % efficiency?

Solution

moles of Cl_2 produced: 106 g – 70 g/mol = 14300 mol Cl_2
faradays of charge: 2 F/mol · 14300 mol = 28600 F
charge in coulombs: 96500 C/mol · 28600 F = $2.76 \cdot 10^9$ C
duration of electrolysis: 3600 s/h · 24 h = 86400 s
current (rate of delivery): $2.76 \cdot 10^9$ A·s − 86400 s = 32300 A
power (A·V): 2 V · 32300 A = 64.6 kW
energy in kW·h: 64.6 kW · 24 h = 1550 kW· h
energy in Joules: 1550 kW·h · 3.6 MJ/kW·h) = 5580 MJ
(In the last step, recall that 1 W = 1 J/s, so 1 kW·h = 3.6 MJ

INDIVIDUAL TEST PAPER

Exercise 1

Make a scheme of galvanic cell from electrodes given in table 6.1.

- Write anodic and cathodic reactions and net process reaction;
- How do the masses of anode and cathode change during the galvanic cell processing?
- What is the direction of electron flow in external circuit?
- Calculate the electromotive force of galvanic cell.

Table 6.1 – Variants of the problem

Variant	Electrodes	Variant	Electrodes
1	Cd^{+2}/Cd Cu^{+2}/Cu	5	Ag^{+}/Ag Al^{+3}/Al
2	Fe^{+2}/Fe Ag^{+}/Ag	6	Mn^{+2}/Mn Sn^{+2}/Sn
3	Sn^{+2}/Sn Al^{+3}/Al	7	Ni^{+2}/Ni Cu^{+2}/Cu
4	Zn^{+2}/Zn Bi^{+3}/Bi	8	Pb^{+2}/Pb Zn^{+2}/Zn
9	Ni^{+2}/Ni Cr^{+3}/Cr	18	Sn^{+2}/Sn Hg^{+2}/Hg
10	Cu^{+2}/Cu Mn^{+2}/Mn	19	Be^{+2}/Be Cr^{+3}/Cr
11	Co^{+2}/Co Be^{+2}/Be	20	Bi^{+3}/Bi Fe^{+2}/Fe
12	Pb^{+2}/Pb Mg^{+2}/Mg	21	Cd^{+2}/Cd Mn^{+2}/Mn
13	Ti^{+2}/Ti Sn^{+2}/Sn	22	Al^{+3}/Al Pb^{+2}/Pb
14	Mn^{+2}/Mn Bi^{+3}/Bi	23	Mg^{+2}/Mg Bi^{+3}/Bi
15	Cd^{+2}/Cd Hg^{+2}/Hg	24	$Mg^{+2}/MgAu^{+}/Au$
16	Cr^{+3}/Cr Co^{+2}/Co	25	Zn^{+2}/Zn Sn^{+2}/Sn
17	Mg^{+2}/Mg Fe^{+2}/Fe	26	Zn^{+2}/Zn Ni^{+2}/Ni

Exercise 2

What electrodes may be used for electrolytic production of gas? Make a scheme of electrolysis (anodic, cathodic, net reaction) and determine parameters of electrolysis for your variant in table 6.2).

Exercise 3

Chose the electrolyte and anodic metal for metal coating formation (table 6.3):

- What are the electrolysis reactions?

- Calculate the electrolysis parameters.

Table 6.2 – Variants of the problem

Variant	Gas	Volume, м^3	Electrolyte	Current, A	Time of electrolysis, hour	Current efficiency, %
1	O_2	3,0	NaOH	5000	?	100
2	H_2	4,1	Na_2SO_4	2000	5,0	?
3	Cl_2	?	NaCl	10000	2,0	90
4	O_2	6,7	KNO_3	?	8,0	100
5	H_2	?	LiOH	3000	10,0	100
6	Cl_2	7,0	$BaCl_2$	8000	?	95
7	O_2	?	?	9000	7,5	100
8	H_2	8,8	?	?	3,5	100
9	Cl_2	6,0	?	4000	4,0	?
10	H_2	8,0	Na_2SO_4	?	2	100
11	Cl_2	10,0	KCl	5000	?	94
12	O_2	?	$MgSO_4$	3500	2,5	100
13	Cl_2	5,2	$CaCl_2$	7000	?	97
14	O_2	12,4	?	?	4	100
15	H_2	?	KOH	4200	5	100
16	O_2	?	Rb_2SO_4	1000	1,5	100
17	H_2	7,3	?	?	3	100
18	Cl_2	3,8	NaCl	2220	4	?
19	H_2	1,5	LiOH	3600	?	100
20	Cl_2	?	$BaCl_2$	4100	2,8	94
21	O_2	?	$Ca(NO_3)_2$	2700	6,5	100
22	Cl_2	4,7	CsCl	?	3	93
23	O_2	9,2	$Ba(NO_3)_2$	3300	?	100
24	H_2	6,5	?	?	4,2	100
25	Cl_2	8,7	NaCl	1000	?	90

Table 6.3 – Variants of the problem

Variant	Metal of coating	Metal density ρ, g/sm^3	Coating thickness δ, mkm	Current density j, A/dm^2	Time of electrolysis, min	Current efficiency, %
1	Ni	8,90	?	1,5	20	90
2	Cd	8,64	7	?	18	98
3	Sn	7,30	9	2,0	10	?
4	Fe	7,87	15	20,0	?	78
5	Cr	7,19	?	8,0	20	30
6	Cu	8,96	3	?	9	100
7	Zn	7,13	12	2,5	21	?
8	Ag	10,50	?	0,8	3	100
9	Au	19,40	1	?	10	100
10	Cd	8,64	6	1,8	?	95
11	Fe	7,87	?	25,0	15	78
12	Cr	7,19	3	6,0	10	?
13	Cu	8,96	5	1,0	?	100
14	Co	8,84	4	?	15	97
15	Zn	7,13	?	1,8	27	87
16	Sn	7,30	8	1,5	?	98
17	Ni	8,90	6	2,5	12	?
18	Ag	10,50	2	1,0	?	100
19	Cd	8,64	?	2,0	12	95
20	Zn	7,13	9	2,0	?	90
21	Fe	7,87	12	15,0	5	?
22	Mn	7,44	?	6,0	9	45
23	Pb	11,33	9	?	8	99
24	Ni	8,90	3	2,0	?	92
25	Sn	7,30	?	1,0	12	96

CHAPTER 7 Corrosion of metals

7.1 The main provisions

Corrosion can be defined as the deterioration of materials by chemical processes. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M - z\bar{e} \rightarrow M^{z+}$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a depolarizer.

In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.

The economic aspects of corrosion are far greater than most people realize; according to a report published in 2001, the cost of corrosion in the U.S. alone was 276 $ billion per year. Of this, about 121 $ billion was spent to control corrosion, leaving the difference of 155 $ billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer the largest economic impact with motor vehicles and transportation being a close second.

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Under normal environmental conditions, the thermodynamically stable states of most of the metallic elements are the cations, rather than the metal itself. This is the reason that considerable energy (and expense) must go into the extraction of a metal from its ore. However, once the metal is won and put into use, it tends to spontaneously revert back to its more stable form. To do so, the metal must lose electrons, and this requires the presence of an electron acceptor or oxidizing agent. Oxygen, of course, is the most prominent of these, but hydrogen ions and the cations of any more "noble" metal[1] are also very common promoters of corrosion.

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. In this sense the system can be regarded as an electrochemical cell in which the anodic process is something like:

$$\mathrm{Fe(s)} - 2\bar{\mathrm{e}} \rightarrow \mathrm{Fe}^{2+}\mathrm{(aq)}$$

and the cathodic steps can be any of:

$$2\,\mathrm{H_2O} + \mathrm{O_2} + 4\bar{\mathrm{e}} \rightarrow 4\,\mathrm{OH}^-$$

$$2\,\mathrm{H}^+ + 2\bar{\mathrm{e}} \rightarrow \mathrm{H_2}$$

A thin film of moisture on the surface of the metal can serve as the medium for the electrolyte.

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic (Fig. 7.1).

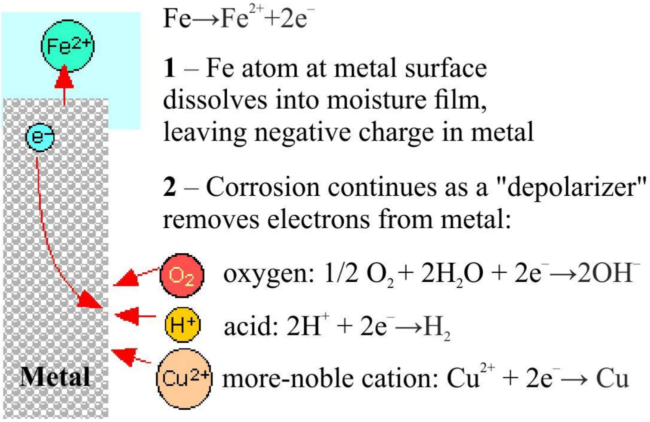


Fig. 7.1 – Electrochemical corrosion of iron

Corrosion often begins at a location where the metal is stressed in some way or isolated from oxygen, such as between joints or under a paint film. The metal ions dissolve in the moisture film and the electrons migrate to another location where they are taken up by a "depolarizer". Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as "rust".

For part of a metal to act as the site for oxidation and dissolution, it must be in contact with the electrolyte, which may be no more than a film of adsorbed moisture. However, practically all metallic surfaces that have been exposed to the atmosphere are coated with a thin film of the metal oxide, which tends to shield the metal from the electrolyte and thus prevent corrosion.

If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this "protected" region will often be the site at which corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.

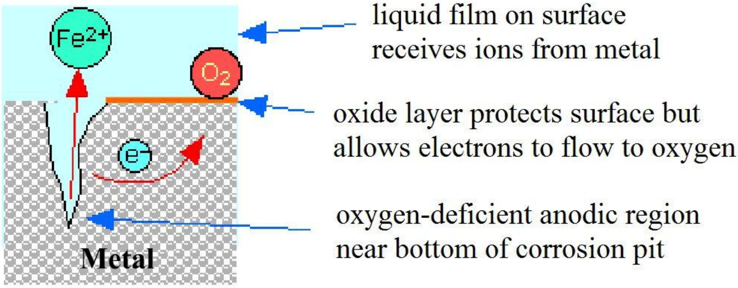


Fig. 7.2 – Pitting corrosion

Most metals are covered with thin layer of oxide film which inhibits anodic dissolution. When corrosion does occur, it sometimes hollows out a narrow hole, or pit, in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal. Many oxides have semiconductive properties and thus do not interfere with the flow of electrons to O_2 (Fig. 7.2).

In contrast to anodic sites, which tend to be localized to specific regions of the surface, the cathodic part of the process can occur almost anywhere. Because metallic oxides are usually semiconductors, most oxide coatings do not inhibit the flow of electrons to the surface, so almost any region that is exposed to O_2 or to some other electron acceptor can act as a cathode.

The tendency of oxygen-deprived locations to become anodic is the cause of many commonly observed patterns of corrosion.

Rusted-out cars and bathroom stains. Anyone who has owned an older car has seen corrosion occur at joints between body parts and under paint films. You will also have noticed that once corrosion starts, it tends to feed on itself. One reason for this is that one of the products of the O_2 reduction reaction is hydroxide ion. The high pH produced in these cathodic regions tends to destroy the protective oxide film, and may even soften or weaken paint films, so that these sites can become anodic. The greater supply of electrons promotes more intense cathodic action, which spawns even more anodic sites, and so on.

A very common cause of corrosion is having two dissimilar metals in contact, as might occur near a fastener or at a weld joint. Moisture collects at the junction point, acting as an electrolyte and forming a cell in which the two metals serve as electrodes. Moisture and conductive salts on the outside surfaces acts as an external conductor, effectively short-circuiting the cell and producing very rapid corrosion; this is why cars rust out so quickly in places where salt is placed on roads to melt ice.

Dissimilar-metal corrosion can occur even if the two metals are not initially in direct contact. For example, in homes where copper tubing is used for plumbing, there is always a small amount of dissolved Cu^{2+} in the water. When this water encounters steel piping or a chrome- plated bathroom sink drain, the more-noble copper will plate out on the other metal, producing a new metals-in-contact corrosion cell. In the case of chrome bathroom sink fittings, this leads to the formation of Cr^{3+} salts which precipitate as greenish stains.

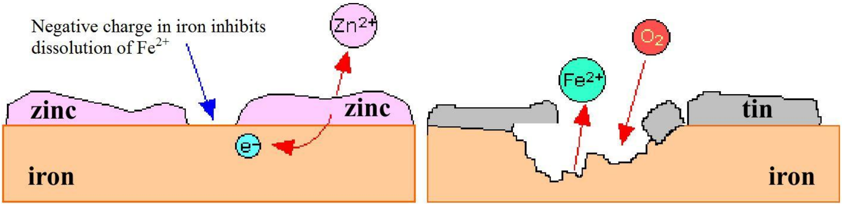
7.2 Control of corrosion

Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion.

The most obvious strategy is to stop both processes by coating the object with paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads.

A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction $M - 2\bar{e} \rightarrow M^{2+}$ to take place.

Sacrificial coatings. One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as ***galvanizing***. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this ***sacrificial coating*** leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.



Sacrificial coatings Noble coatings

Fig. 7.3 – Corrosion protection by sacrificial coating, and its reverse

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron. You have probably observed how tin cans disintegrate very rapidly when left outdoors.

Cathodic protection. Another way of keeping metal in a cathodic state is to connect it to an external direct current source. For smaller structures such as boats and domestic water water heaters the current is supplied by a sacrificial anode made of aluminum or zinc. For larger extended structures such as piers and buried pipelines, an external line-operated or photovoltaic power supply is commonly used. (All interstate oil piplines in the U.S. are required by law to employ cathodic protection.)

CONCEPTS TO REMEMBER

Corrosion is the gradual destruction of materials, (usually metals), by chemical reaction with its environment.

Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact and immersed in an electrolyte.

Cathodic protection is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell.

Pitting corrosion is a form of extremely localized corrosion that leads to the creation of small holes in the metal.

Passivation refers to the spontaneous formation of an ultra thin film of corrosion products known aspassive film, on the metal's surface tha tactas a barrier to further oxidation. The chemical composition and microstructure of a passive film are different from the underlying metal.

INDIVIDUAL TEST PAPER

Exercise 1

Write the anodic and cathodic reactions occurring under corrosion of metal given in your variant (table 7.1) in the presence of oxygen in different media:

- neutral (pH = 7);
- acidic (pH = 3);
- alkali (pH = 10).

Table 7.1 – Variants of the problem

Variant	Metals	Variant	Metals	Variant	Metals
1	Li, Zn, Ag	9	Mg, Co, Re	17	Ba, Zn, Sb
2	Na, Cd, Cu	10	Sr, Ni, Cu	18	Ca, Cr, Re
3	Ba, Fe, Hg	11	Ca, Mo, Ru	19	Na, Ga, Cu
4	Ca, Ni, Au	12	Rb, Sn, Rh	20	Sr, Fe, Hg
5	Sr, Mn, Bi	13	Li, Pb, Ag	21	Cs, In, Ag
6	K, Co, Pd	14	Be, W, Os	22	Rb, Mn, Tc
7	Cs, Cd, Sb	15	Mg, Al, Pd	23	Li, Ti, Ru
8	Ba, Tl, Bi	16	K, Mn, Ge	24	Sr, Pb, Ge

PART II ORGANIC CHEMISTRY

CHAPTER 8

Introduction to organic chemistry: alkanes, cycloalkanes and alkyl halides

8.1 Organic and inorganic compounds

During the latter part of the eighteenth century and the early part of the nineteenth century, chemists began to categorize compounds into two types: organic and inorganic. Compounds obtained from living organisms were called organic compounds, and compounds obtained from mineral constituents of the earth were called inorganic compounds.

During this early period, chemists believed that a special "vital force" supplied by a living organism was necessary for the formation of an organic compound. This concept was proved incorrect in 1828 by the German chemist Fredrick Wohler. Wohler heated an aqueous solution of two inorganic compounds, ammonium chloride and silver cyanide, and obtained urea (a component of urine):

$$\mathrm{NH_4Cl + AgNCO \rightarrow (NH_2)_2\,CO + AgCl} \qquad (8.1)$$

The terms organic and inorganic continue to be used in classifying compounds, but the definitions of these terms no longer reflect their historical origins. Organic chemistry is the study of hydrocarbons (compounds of carbon and hydrogen) and their derivatives. Nearly all compounds found in living organisms are still classified as organic compounds, as are many compounds that have been synthesized in the laboratory and have never been found in a living organism. Inorganic chemistry is the study of all substances other than hydrocarbons and their derivatives.

8.2 Classification of organic compounds

The field of organic chemistry encompasses the study of hydrocarbons and hydrocarbon derivatives. A hydrocarbon is a compound that contains only carbon atoms and hydrogen atoms. Thousands of hydrocarbons are known. A hydrocarbon derivative is a compound that contains carbon and hydrogen and one or more additional elements. Additional elements commonly found in hydrocarbon derivatives include O, N, S, P, F, CI, and Br. Millions of hydrocarbon derivatives are known.

Hydrocarbons may be divided into two large classes: saturated and unsaturated. A saturated hydrocarbon is a hydrocarbon in which all carbon-carbon bonds are single bonds. Saturated hydrocarbons are the simplest type of organic compound. An unsaturated hydrocarbon is a hydrocarbon in which one or more carbon-carbon multiple bonds (double bonds, triple bonds, or both) are present. In general, saturated and unsaturated hydrocarbons undergo distinctly different chemical reactions. Saturated hydrocarbons are the subject of this chapter. Unsaturated hydrocarbons are considered in the chapter 9. Figure 8.1 summarizes the terminology presented.

Two categories of saturated hydrocarbons exist, those with ***acyclic*** carbon atom arrangements and those with ***cyclic*** carbon

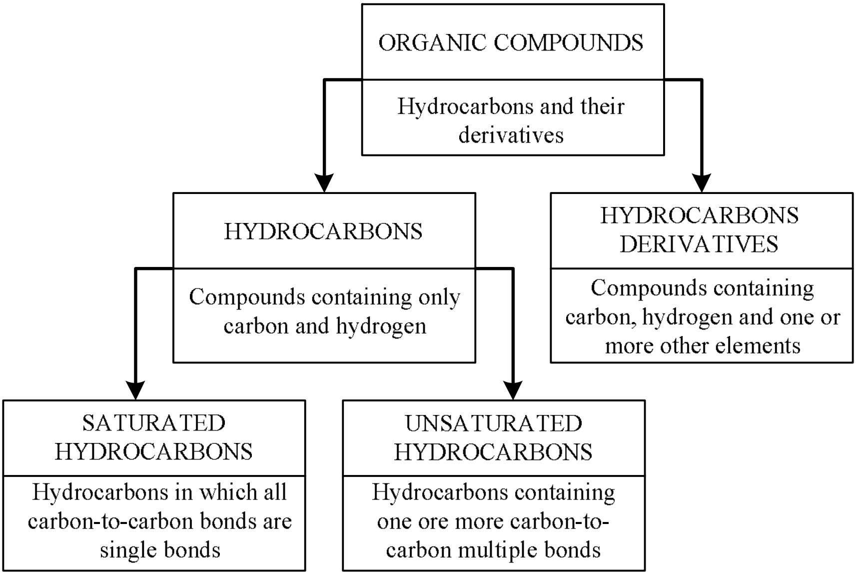
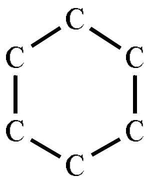


Fig. 8.1 – Classification of organic compounds

atom arrangements. The term acyclic means "not cyclic." The following notations contrast simple acyclic and cyclic arrangements of six-carbon atoms:

$$C-C-C-C-C-C$$

Acyclic



Cyclic

8.3 Condensed formulas, complete and skeletal structures

Two-dimensional structural representations for organic molecules are called structural formulas. A structural formula is a two-dimensional structural representation that shows the various atoms in a molecule are bonded to each other. Structural formulas are of two types: expanded structural formulas and condensed structural formulas. An expanded structural formula is a structural formula that shows all atoms in a molecule and all bonds connecting the atoms. When written out, expanded structural formulas generally occupy a lot of space, and condensed structural formulas represent a shorthand method for conveying the same information. A condensed structural formula is a structural formula that uses groupings of atoms, in which central atoms and the atoms connected to them are written as a group, to convey molecular structural information.

In situations where the focus is solely on the arrangement of carbon atoms in a compound, skeletal structural formulas that omit the hydrogen atoms are often used. A skeletal structural formula is a structural formula that shows the arrangement and bonding of carbon atoms present in an organic molecule but does not show the hydrogen atoms attached to the carbon atoms. The expanded (*a*), condensed (*b*) and skeletal (*c*) structural formulas for propane follow (Fig. 8.2).

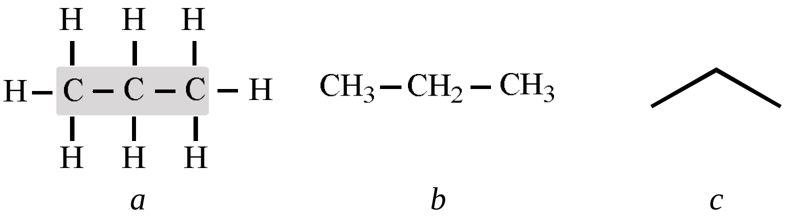


Fig. 8.2 – Type of formulas for propane: *a* – expanded; *b* – skeletal; *c* – structural.

8.4 Physical properties of alkanes and cycloalkanes

1. Alkanes and cycloalkanes are in soluble in water. Water molecules are polar, and alkane and cycloalkane molecules are nonpolar. Molecules of unlike polarity have limited solubility in one another. The water in solubility of alkanes makes them good preservatives for metals.

2. Alkanes and cycloalkanes have densities lower than that of water. Alkane and cycloalkane densities fall in the range 0.6 g/ml to 0.8 g/ml, compared with water's density of 1.0 g/ml. When alkanes and cycloalkanes are mixed with water, two layers form (due to the solubility) with the hydrocarbon layer on top (because of its lower density). This density difference between alkanes/cycloalkanes and water explains why oil pills in aqueous environments spread so quickly.

3. The boiling points of continuous-chain alkanes and cycloalkanes increase with an increase in carbon chain length or ring size. For continuous-chain alkanes, the boiling pointing creases roughly 30 ºC for every carbon atom added to the chain.

8.5 Chemical properties of alkanes and cycloalkanes

Alkanes are the least reactive type of organic compound. They can be heated for long periods of time in strong acids and bases with no appreciable reaction. Strong oxidizing agent sand reducing agents have little effect on alkanes. Alkanes are not absolutely unreactive. Two important reactions that they undergo are combustion, which is reaction with oxygen, and halogenation, which is reaction with halogens.

1. Combustion. A combustion reaction is a chemical reaction between a substance and oxygen (usually from air) that proceeds with the evolution of heat and light (usually as a flame). Alkanes readily undergo combustion when ignited. When sufficient oxygen is present to support total combustion, carbon dioxide and water are the products:

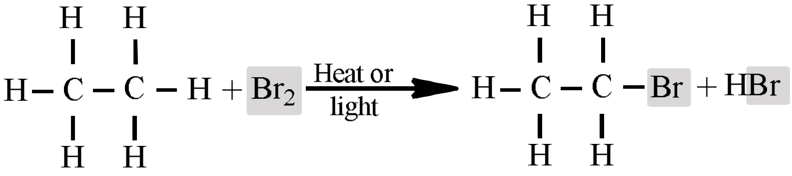
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat energy} \tag{8.2}$$

$$2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O + \text{heat energy} \tag{8.3}$$

The exothermic nature of alkane combustion reactions explains the extensive use of alkanes as fuels. Natural gas, used in home heating, is predominantly methane. Propane is used in home heating in rural areas and in gas barbecue units. Butane fuels are portable camping stoves. Gasoline is a complex mixture of many alkanes and other types of hydrocarbons.

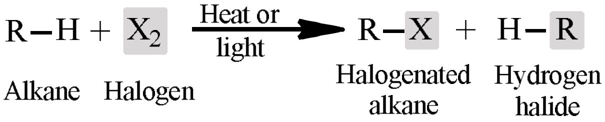
2. Halogenation. The halogens are the elements in Group VIIA of the periodic table: fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). A halogenation reaction is a chemical reaction between a substance and a halogen in which one or more halogen atoms are incorporated into molecules of the substance.

Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms. An example of an alkane halogenation reaction is:



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H + Br_2 \xrightarrow[\text{light}]{\text{Heat or}} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Br + HBr$$

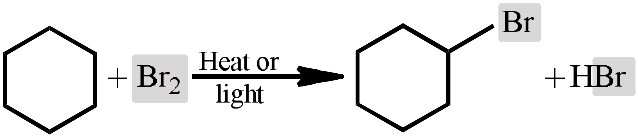
A general equation for the substitution of a single halogen atom for one of the hydrogen atoms of an alkane is:



$$\underset{\text{Alkane}}{R-H} + \underset{\text{Halogen}}{X_2} \xrightarrow[\text{light}]{\text{Heat or}} \underset{\text{Halogenated alkane}}{R-X} + \underset{\text{Hydrogen halide}}{H-R}$$

In halogenation of an alkane, the alkane is said to undergo fluorination, chlorination, bromination, or iodination, depending on the identity of the halogen reactant. Chlorination and bromination are the two widely used alkane halogenation reactions. Fluorination reactions generally proceed too quickly to be useful, and iodination reactions go too slowly.

The chemical properties of cycloalkanes are similar to those of alkanes. Cycloalkanes readily undergo combustion as well as chlorination and bromination (reaction 8.4). With unsubstituted cycloalkanes, monohalogenation produces a single product because all hydrogen atoms present in the cycloalkane are equivalent to one another.



(8.4)

A halogenated alkane is an alkane derivative in which one or more halogen atoms a represent. Similarly, a halogenated cycloalkane is a cycloalkane derivative in which one or more halogen atoms a represent. Produced by halogenation reactions, these two types of compounds represent the first class of hydrocarbon derivatives that we formally consider in this text.

8.6 Physical properties of alkyl halides

The physical properties of alkyl halides considerably differ from those of the corresponding alkanes. The strength and length of the carbon-halogen bond (C–X bond), the dipole moment and the boiling point of an alkyl halide are determined by the polarity of the bond as well as by the size of the various halogen atoms.

1. The C–X bond strength decreases with an increase of the size of the halogen (X) because the size of the *p*- orbital of the halogen increases as well. Thus, the *p*- orbital becomes more diffused and the overlap with the orbital of the carbon deteriorates. As a result, the C–X bond is weakened and elongated.

2. Halogens (F_2, Cl_2 and Br_2) are more electronegative than carbon. Consequently, carbon atoms that carry halogens are charged partially positive while the halogen is charged partially negative. The polarity of the C–X bond causes a measurable dipole moment. As a result of the partial positive charge, the carbon atom displays an electrophilic character. The chemical behavior of alkyl halides is determined mainly by the electrophilicity of the carbon.

3. The boiling points of alkyl halides are considerably higher than those of the corresponding alkanes. The main reason for this is the dipole moment of alkyl halides, which leads to attractive dipole-dipole interactions in liquid alkyl halides.

8.7 Chemical properties of alkyl halides

Fundamentally, organic compounds that contain a carbon with a more electronegative substituent display two types of reactions: nucleophilic substitution reactions and elimination reactions. In nucleophilic substitutions, the electronegative substituent (leaving group) is exchanged (substituted) for another substitutent (nucleophile). In eliminations, however, the electronegative substituent is released from the organic molecule along with another atom or group which is usually a hydrogen from the vicinal carbon atom.

Alkyl halides (R–X) are representative examples of such organic compounds. The leaving groups in nucleophilic substitutions and eliminations with alkyl halides are the halide anions (X–) Cl–, Br– and I–. F– virtually never functions as a leaving group (Fig. 8.3).

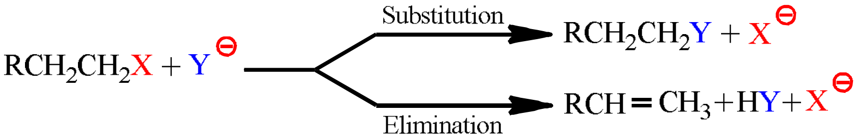


Fig.8.3 – Reaction types of alkyl halides

Substitution reactions are particularly useful in organic chemistry because they enable synthetically easily available alkyl halides to be converted into multiple other organic compounds.

CONCEPTS TO REMEMBER

Carbon atom bonding characteristics. Carbon atoms in organic compounds must have four bonds.

Types of hydrocarbons. Hydrocarbons, binary compounds of carbon and hydrogen, are of two types: saturated and unsaturated. In saturated hydrocarbons, all carbon–carbon bonds are single bonds. Unsaturated hydrocarbons have one or more carbon–carbon multiple bonds−double bonds, triple bonds, or both.

Alkanes. Alkanes are saturated hydrocarbons in which the carbon atom arrangement is that of an unbranched or branched chain. The formulas of all alkanes can be represented by the general formula C_nH_{2n+2}, where n is the number of carbon atoms present.

Structural formulas. Structural formulas are two-dimensional representations of the arrangement of the atoms in molecules. These formulas give complete information about the arrangement of the atoms in a molecule but not the spatial orientation of the atoms. Two types of structural formulas are commonly encountered: expanded and condensed.

Isomers. Isomers are compounds that have the same molecular formula, (that is, the same numbers and kinds of atoms) but that differ in the way the atoms are arranged.

Cycloalkanes. Cycloalkanes are saturated hydrocarbons in which at least one cyclic arrangement of carbon atoms is present. The formulas of all cycloalkanes can be represented by the general formula CnH2n, where n is the number of carbon atoms present.

Cycloalkane nomenclature. The IUPAC name for a cycloalkane is obtained by placing the prefix cyclo- before the alkane name that corresponds to the number of carbon atoms in the ring. Alkyl groups attached to the ring are located by using a ring-numbering system.

Halogenated alkanes. Halogenated alkanes are hydrocarbon derivatives in which one or more halogen atoms have replaced hydrogen atoms of the alkane.

Halogenated alkane nomenclature. Halogenated alkanes are named by using the rules that apply to branched-chain alkanes, with halogen substituents being treated the same as alkyl groups.

INDIVIDUAL TEST PAPER

Exercise 1

Identify the following as formulas of organic or inorganic compounds in the table 8.1.

Table 8.1 – Variants of the problem

Variant	Compounds
1	KCl, C_3H_7Cl, C_2H_6S, $C_6H_5CH_3$
2	C_6H_{12}, $MgSO_4$, $CaCl_2$, $C_6H_{12}O_6$
3	NaCNS, $C_6H_5CH_3$, $CaCO_3$, $NaHCO_3$
4	C_6H_6, H_2SO_4, C_3H_7Cl, C_2H_6S
5	C_4H_{10}, KCl, $C_{10}H_{22}$,KCN
6	C_2H_4, $CaCO_3$, $CaCl_2$, C_4H_{10}
7	$C_{10}H_{22}$, C_6H_6, C_3H_7Cl, C_6H_{12}
8	$MgSO_4$, $C_{10}H_{22}$, KCN, $NaHCO_3$
9	NaCNS, $C_{10}H_{22}$, C_2H_6O, $C_6H_{12}O_6$
10	C_2H_6O, $CaCO_3$, C_2H_4, C_4H_{10}
11	$CaCl_2$, $NaHCO_3$, C_6H_6, C_6H_{12}
12	CH_4,C_2H_6S, H_2SO_4, C_2H_6O
13	$NaHCO_3$, $C_6H_{12}O_6$, C_2H_6O, C_2H_4
14	C_6H_{12}, $CaCO_3$, CH_4, NaCNS

Exercise 2

Convert each condensed formula to a complete and skeletal structure (table 8.2).

Table 8.2 – Variants of the problem

Variant	Compounds
1	$(CH_3)_2CHCH_2CH_3$, C_5H_{10} (cyclopentane)
2	$(CH_3)_2CHCH_2CH(CH_3)_2$, C_6H_{12}(cyclohexane)
3	$CH_3(CH_2)_5CH_3$, C_3H_6 (cyclopropane)
4	$CH_3C(CH_3)_3$, C_4H_8 (cyclobutane)
5	$(CH_3)_2CHCH_3$, C_5H_{10} (cyclopentane)
6	$(CH_3)_2CHCH(CH_3)_2$, C_6H_{12} (cyclohexane)
7	$CH_3CH(CH_3)_2$, C_4H_8 (cyclobutane)
8	$(CH_3)_2CHCH_2CH_3$, C_3H_6 (cyclopropane)
9	$CH_3CH_2CH(CH_3)_2$, C_8H_{16} (cyclooctane)
10	$CH_3CH_2CH(CH_3)_2$, C_6H_{12} (cyclohexane)
11	$(CH_3)_3CCH_2C(CH_3)_3$, C_4H_8 (cyclobutane)
12	$(CH_3)_2CHCH_3$, C_3H_6 (cyclopropane)
13	$CH_3(CH_2)_3CH(CH_3)_2$, C_4H_8 (cyclobutane)
14	$CH_3(CH_2)_2C(CH_3)_3$, C_8H_{16} (cyclooctane)

Exercise 3

Write a balanced equation for the complete combustion of an alkane given in the table 8.3.

Table 8.3 – Variants of the problem

Variant	Alkane	Variant	Alkane
1	$CH_3(CH_2)_3CH(CH_3)_2$	5	$CH_3CH(CH_3)_2$
2	$CH_3(CH_2)_2C(CH_3)_3$	6	$CH_3CH_2CH(CH_3)_2$
3	$(CH_3)_3CCH_2C(CH_3)_3$	7	$(CH_3)_2CHCH(CH_3)_2$
4	$(CH_3)_2CHCH_3$	8	$CH_3CH(CH_3)_2$

Continued of table 8.3

Variant	Alkane	Variant	Alkane
9	$CH_3C(CH_3)_3$	12	$(CH_3)_2CHCH_2CH(CH_3)_2$
10	$(CH_3)_2CHCH_3$	13	$CH_3(CH_2)_5CH_3$
11	$(CH_3)_2CHCH_2CH_3$	14	$CH_3(CH_2)_3CH(CH_3)_2$

Exercise 4

Give (table 8.4):

- the IUPAC name for each of the following branched-chain alkanes;
- the major product(s) of the UV-induced halogenation reactions of alkane.

Table 8.4 – Variants of the problem

Variant	Alkane	Variant	Alkane
1	$(CH_3)_2CHCH_2CH(CH_3)_2$	4	$(CH_3)_2CHCH_2CH_3$
2	$CH_3(CH_2)_3CH(CH_3)_2$	5	$CH_3C(CH_3)_3$
3	$(CH_3)_2CHCH_2CH(CH_3)_2$	6	$(CH_3)_2CHCH_3$
7	$(CH_3)_2CHCH(CH_3)_2$	11	$CH_3CH(CH_3)_2$
8	$CH_3CH(CH_3)_2$	12	$(CH_3)_2CHCH_3$
9	$CH_3(CH_2)_3CH(CH_3)_2$	13	$CH_3(CH_2)_2C(CH_3)_3$
10	$(CH_3)_2CHCH(CH_3)_2$	14	$(CH_3)_2CHCH_2CH_3$

Exercise 5

How will you prepare vinyl chloride? Complete the reaction of vinyl chloride with substances given in the table 8.5.

Table 8.5 – Variants of the problem

Variant	Compounds
1	H_2O, KOH
2	Cl_2
3	HBr
4	C_2H_5OH, KOH, boiling
5	C_2H_5OH, KOH, ambient conditions
6	H_2O, KOH, hydrolysis
7	HBr
8	H_2O, KOH, hydrolysis
9	C_2H_5OH, KOH, ambient conditions
10	C_2H_5OH, KOH, boiling
11	Cl_2
12	C_2H_5OH
13	C_2H_5OH, KOH, boiling
14	HCl

Exercise 6

Write a balanced equation for the reaction between reactants given in the table 8.6.

Table 8.6 – Variants of the problem

Variant	Compounds
1	$CH_3CH_2CH_2CH_2Br + KOH_{(alcoholic)} \rightarrow$
2	$CH_3CH_2CH_2CH_2Br + NaNH_2 \rightarrow$
3	$CH_3CH_2CH_2CH_2Br + NaOH_{(alcoholic)} \rightarrow$
4	$CH_3CH_2CH_2CH_2Br + KNH_2 \rightarrow$
5	$CH_3CH_2Br + CH_3(CH_2)_3Br + Na_{(ether)} \rightarrow$

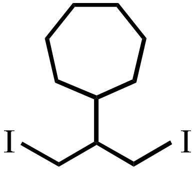
Table 8.6 – Variants of the problem

Variant	Compounds
6	$CH_3CH_2Br + Na_{(ether)} \rightarrow$
7	$CH_3CH_2Br + CH_3Br + Na_{(ether)} \rightarrow$
8	$CH_3Br + Na_{(ether)} \rightarrow$
9	$CH_3Br + Li_{(ether)} \rightarrow$
10	$CH_3CH_2CH_2Br + Mg_{(ether)} \rightarrow$
11	$CH_3CH_2CH_2Br + Li_{(ether)} \rightarrow$
12	$CH_3CH_2CH_2Br + Zn_{(ether)} \rightarrow$
13	$CH_3CH_2Br + NaPb_{(ether)} \rightarrow$
14	$CH_3CH_2CH_2CH_2Br + KOH_{(alcoholic)} \rightarrow$

Exercise 7

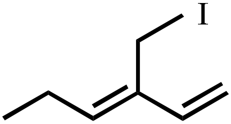
Match the name for each of the following alkyl halides and organometallic compounds with the formula (table 8.7).

Example:

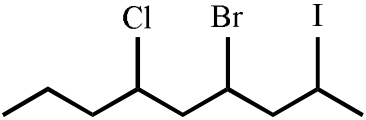
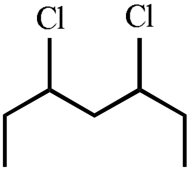
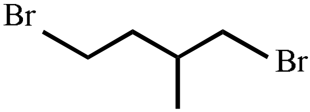
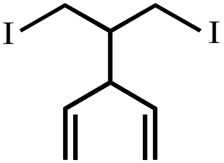
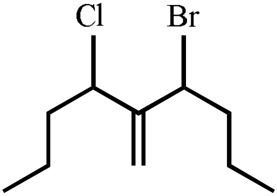
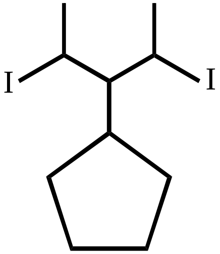


(1,3-diiodo-propane-2-yl)-cycloheptane

Table 8.7 – Variants of the problem

IUPAC name	Formula
2-(1-chlorobutyl)-3-bromohex-1-ene	

Continued of table 8.7

IUPAC name	Formula
2,4-diiodopentan-3-yl-cyclopentane	
3-(1,3-diiodopropan-2-yl)-penta-1,4-diene	
3-Iodomethyl-hexa-1,3-diene	
4-Bromo-6-chloro-2-iodo-nonane	
3,5-Dichloro-heptane	
1,4-Dibromo-2-methyl-butane	

CHAPTER 9

Unsaturated hydrocarbons: alkenes, dienes, alkynes

9.1 Unsaturated hydrocarbons

An unsaturated hydrocarbon is a hydrocarbon in which one or more carbon–carbon multiple bonds (double bonds, triple bonds, or both) are present. Unsaturated hydrocarbons have physical properties similar to those of saturated hydrocarbons. However, their chemical properties are much different. Unsaturated hydrocarbons are chemically more reactive than their saturated counterparts. The increased reactivity of unsaturated hydrocarbons is related to the presence of the carbon–carbon multiple bond(s) in such compounds.

These multiple bonds serve as locations where chemical reactions can occur. Whenever a specific portion of a molecule governs its chemical properties, that portion of the molecule is called a functional group. A functional group is the part of an organic molecule where most of its chemical reactions occur. Carbon–carbon multiple bonds are the functional group for an unsaturated hydrocarbon.

The study of various functional groups and their respective reactions provides the organizational structure for organic chemistry. Each of the organic chemistry chapters that follow introduces new functional groups that characterize families of hydrocarbon derivatives.

Unsaturated hydrocarbons are subdivided into three groups on the basis of the type of multiple bond(s) present: ***alkenes***, which contain one or more carbon–carbon double bonds; ***alkynes***, which contain one or more carbon–carbon triple bonds, and ***aromatic hydrocarbons***, which exhibit a special type of "delocalized" bonding that involves a six-membered carbon ring. We begin our consideration of unsaturated hydrocarbons with a discussion of alkenes. Information about alkynes and aromatic hydrocarbons then follows.

9.2 Characteristics of alkenes and cycloalkenes

An alkene is an cyclic unsaturated hydrocarbon that contains one or more carbon–carbon double bonds. The alkene functional group is, thus, a C=C group. Note the close similarity between the family names alkene and alkane; they differ only in their endings: ***-ene*** versus ***-ane***. The -ene ending means a double bond is present. The simplest type of alkene contains only one carbon–carbon double bond. Such compounds have the general molecular formula $\mathbf{C_nH_{2n}}$. Thus alkenes with one double bond have two fewer hydrogen atoms than do alkanes (C_nH_{2n+2}).

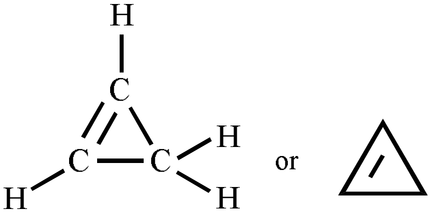
The two simplest alkenes are ethene (C_2H_4) and propene (C_3H_6):

$$CH_2{=}CH_2 \qquad\qquad CH_2{=}\,CH{-}CH_3$$

Ethene Propene

A cycloalkene is a cyclic unsaturated hydrocarbon that contains one or more carbon–carbon double bonds within the ring system. Cycloalkenes in which there is only one double bond have the general molecular formula $\mathbf{C_nH_{2n-2}}$. This general formula reflects the loss off our hydrogen atoms from that of an alkane (C_nH_{2n+2}). Note that two hydrogen atoms are lost because of the double bond and two because of the ring structure.

The simplest cycloalkene is the compound cyclopropene (C_3H_4), a three-membered carbon ring system containing one double bond:



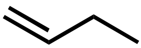
Cyclopropene

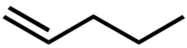
Alkenes with more than one carbon–carbon double bond are relatively common. When two double bonds are present, the compounds are often called ***dienes***; for three double bonds the designation ***trienes*** is used. Cycloalkenes that contain more than one double bond are possible but are not common.

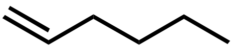
9.3 Line-angle structural formulas for alkenes

Line-angle formulas for the three- to six- carbon acyclic 1-alkenes are as follows:

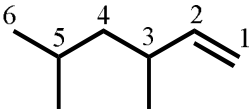

Propene


1-Butane

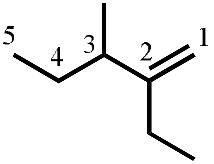

1-Pentene


1-Hexene

Representative line-angle structural formulas for substituent-bearing alkenes include:

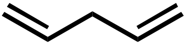


3,5-Dimethyl-1-hexen

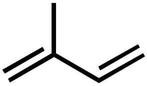


2-Ethyl-3-methyl-1-pentene

Diene representations in terms of line-angle structural formulas include:



1,4-Pentadiene



2-Methyl-1,3-butadiene

9.4 Physical and chemical properties of alkenes

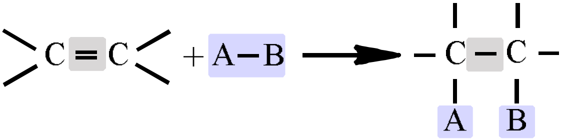
Alkenes show similar properties as alkanes. The density is less than that of water (0.6 – 0.8 g/cm^3). They are immiscible with water but easily dissolve in alcohols and ether. At room temperature, ethene, propene and butene are gaseous while higher, unbranched alkenes are liquids. Starting with 16 °C atoms, alkenes are solids.

Alkenes, like alkanes, are very flammable. The combustion products, as with any hydrocarbon, are carbon dioxide and water.

$$C_2H_4(\text{Ethene}) + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad (9.1)$$

Aside from combustion, nearly all other reactions of alkenes take place at the carbon–carbon double bond(s). These reactions are called addition reactions because a substance is added to the double bond. This behavior contrasts with that of alkanes, where the most common reaction type, aside from combustion, is substitution.

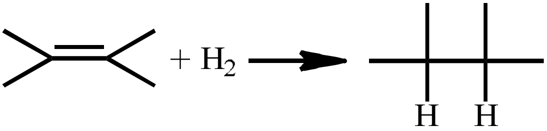
An addition reaction (9.2) is a reaction in which atoms or groups of atoms are added to each carbon atom of a carbon–carbon multiple bond in a hydrocarbon or hydrocarbon derivative. A general equation for an alkene addition reaction is:



(9.2)

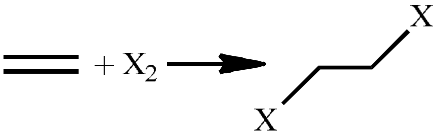
In this reaction, the A part of the reactant A–B becomes attached to one carbon atom of the double bond, and the B part to the other carbon atom. As this occurs, the carbon–carbon double bond simultaneously becomes a carbon–carbon single bond.

A hydrogenation reaction (9.3) is an addition reaction in which H_2 is incorporated into molecules of an organic compound. In alkene hydrogenation a hydrogen atom is added to each carbon atom of a double bond. It is accomplished by heating the alkene and H_2 in the presence of a catalyst (usually Ni or Pt).



(9.3)

A halogenation reaction (9.4) is an addition reaction in which a halogen is incorporated into molecules of an organic compound. In alkene halogenation a halogen atom is added to each carbon atom of a double bond. Chlorination (Cl_2) and bromination (Br_2) are the two halogenation processes most commonly encountered. No catalyst is needed.

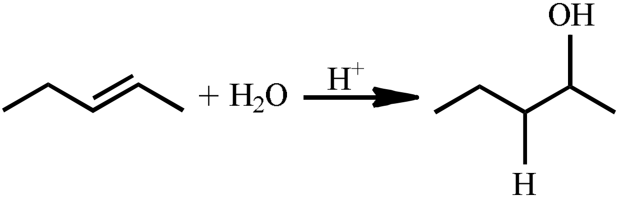


(9.4)

A hydrohalogenation reaction is an addition reaction in which a hydrogenhalide (HCl, HBr, or HI) is incorporated into molecules of an organic compound. In alkene hydrohalogenation one carbon atom of a double bond receives a halogen atom and the other carbon atom receives a hydrogen atom. Hydrohalogenation reactions require no catalyst.

Markovnikov's rule states that when an unsymmetrical molecule of the form H_2O adds to an unsymmetrical alkene, thehydrogen atom from the H_2O becomes attached to the unsaturated carbon atom that already has the most hydrogen atoms.

A hydration reaction (9.5) is an addition reaction in which H_2O is incorporated into molecules of an organic compound. In alkene hydration one carbon atom of a double bond receives a hydrogen atom and the other carbon atom receives an – OH group. Alkene hydration requires a small amount of H_2SO_4 (sulfuric acid) as a catalyst. For symmetrical alkenes, only one product results from hydration:



(9.5)

Polymerization is another addition reaction of alkenes. This important technical reaction occurs by a catalyzed radical mechanism and provides access to important industrial products such as polyethylene from ethene and polypropylene from propylene:

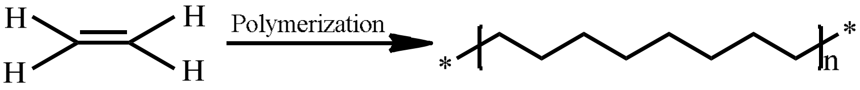


Fig.9.1 – Polymerization of ethylene

9.5 Alkynes

Alkynes represent the second class of unsaturated hydrocarbons. An alkyne is an acyclic unsaturated hydrocarbon that contains one or more carbon–carbon triple bonds. The alkyne functional group is, thus, a C≡C group. As the family name alkyne indicates, the characteristic “ending” associated with a triple bond is ***-yne***.

The general formula for an alkyne with one triple bond is $\mathbf{C_nH_{2n-2}}$. Thus the simplest member of this type of alkyne has the formula C_2H_2, and the next member, with n = 3, has the formula C_3H_4.

$CH \equiv CH$	$CH \equiv C-CH_3$
Ethyne	Propyne

9.6 Physical and chemical properties of alkynes

The physical properties of alkynes are similar to those of alkenes and alkanes. In general, alkynes are insoluble in water but soluble in organic solvents, have densities less than that of water, and have boiling points that increase with molecular mass. Low-molecular-mass alkynes are gases at room temperature.

The triple-bond functional group of alkynes behaves chemically quite similarly to the double-bond functional group of alkenes. Thus there are many parallels between alkene chemistry and alkyne chemistry. The same substances that add to double bonds (H_2, HCl, Cl_2, and so on) also add to triple bonds. However, two molecules of a specific reactant can add to a triple bond, as contrasted to the addition of one molecule of reactant to a double bond. In triple-bond addition, the first molecule converts the triple bond into a double bond, and the second molecule then converts the double bond into a single bond. For example, propyne reacts with H_2 to form propene first and then to form propane:

$$CH \equiv C-CH_3 \xrightarrow[Ni]{H_2} CH_2 = CH-CH_3 \xrightarrow[Ni]{H_2} CH_3-CH_2-CH_3$$

An alkyne (propyne)	An alkene (propene)	An alkane (propane)

Alkynes, like alkenes and alkanes, are flammable, that is, they readily undergo combustion reactions.

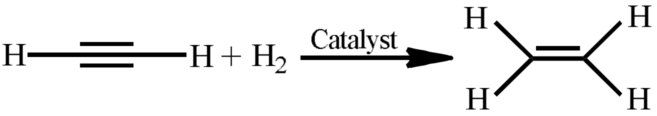
1. Combustion of ethyne (acetylene):

$$H\equiv H + 2.5\ O_2 \longrightarrow 2\ CO_2 + H_2O \qquad (9.6)$$

Since the heat of combustion of ethyne is distributed over only three molecules of gases produced, the flame temperature (above 2500 °C) is very high. Therefore, acetylene is frequently used for welding purposes.

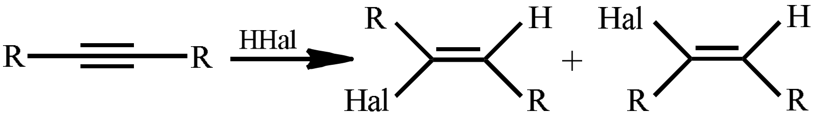
2. Hydrogenation of ethyne to ethane. During the catalytic hydrogenation of ethyne, ethene is formed first which in the next step is further reduced to ethane (reaction 9.7). In this reaction, the

heat of hydrogenation of the first π bond is higher than that of the second. Internal alkynes are more stable than terminal ones as exemplified by the heat of hydrogenation of isomeric butynes to butane.



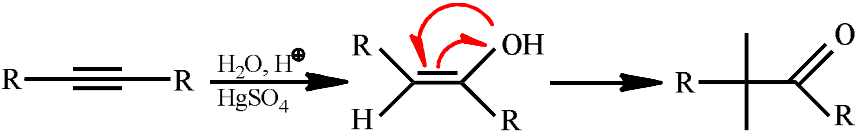
(9.7)

3. Addition of hydrogen halides to alkynes:



The high electron density of the triple bond favors attack by electrophiles following the Markovnikov rule.

4. Hydration of alkynes:



Catalyzed by mercury (II) salts, water can be added to alkynes according to the Markovnikov rule. This reaction yields enoles which tautomerize to the corresponding carbonyl compounds.

CONCEPTS TO REMEMBER

Unsaturated hydrocarbons. An unsaturated hydrocarbon is a hydrocarbon that contains one or more carbon–carbon multiple bonds. Three main classes of unsaturated hydrocarbons exist: alkenes, alkynes, and aromatic hydrocarbons.

Alkenes and cycloalkenes. An alkene is an acyclic unsaturated hydrocarbon in which one or more carbon–carbon double bonds a represent. A cycloalkene is a cyclic unsaturated hydrocarbon that contains one or more carbon–carbon double bonds within the ring system.

Alkene nomenclature. Alkenes and cycloalkenes are given IUPAC names using rules similar to those for alkanes and cycloalkanes, except that the ending -ene is used. Also, the double bond takes precedence both in selecting and in numbering the main chain or ring.

Cis–trans isomerism in alkenes. Cis–trans isomerism is possible for some alkenes because there is restricted rotation about a carbon–carbon double bond.

Addition reactions of alkenes. Numerous substances, including H_2, Cl_2, Br_2, HCl, HBr, and H_2O, add to an alkene carbon–carbon double bond. When both the alkene and the substance to be added are unsymmetrical, the addition proceeds according to Markovnikov's rule: The carbon atom of the double bond that already has the greater number of H atoms gets one more.

Addition polymers. Addition polymers are formed from alkene monomers that undergo repeated addition reactions with each other. Many familiar and widely used materials, such as fibers and plastics, are addition polymers.

INDIVIDUAL TEST PAPER

Exercise 1

Identify the following as formulas of alkanes, alkenes or alkynes in the table 9.1.

Table 9.1 – Variants of the problem

Variant	Compounds
1	$C_{14}H_{28}$, C_4H_{10}, C_3H_6, C_3H_6
2	C_6H_{12}, C_4H_{10}, $C_{10}H_{18}$, C_3H_8
3	C_5H_{12}, C_4H_6, $C_{11}H_{24}$, C_3H_8
4	C_6H_{12},C_3H_8, C_2H_6, $C_{10}H_{20}$
5	C_4H_{10}, $C_{10}H_{20}$, C_2H_4, C_3H_6
6	C_2H_4, C_4H_{10}, $C_{11}H_{24}$, C_3H_8
7	$C_{10}H_{22}$, C_6H_{10} ,C_3H_4 , C_6H_{12}
8	C_2H_6 , C_6H_{12} ,C_3H_6 , C_6H_{14}
9	C_3H_6 , $C_{14}H_{30}$,$C_{15}H_{28}$, C_4H_{10}
10	C_4H_6 , $C_{13}H_{26}$,$C_{14}H_{28}$, C_5H_{12}
11	C_5H_{10} , $C_{12}H_{22}$,$C_{13}H_{28}$, C_6H_{14}
12	C_6H_{14} , $C_{11}H_{22}$,$C_{12}H_{22}$, C_7H_{16}
13	C_7H_{14} , $C_{10}H_{22}$,$C_{11}H_{22}$, C_8H_{18}
14	C_8H_{14} , C_9H_{18} ,$C_{10}H_{18}$, C_9H_{16}

Exercise 2

Convert each condensed formula to a complete and skeletal structure (table 9.2.)

Table 9.2 – Variants of the problem

Variant	Compounds	Variant	Compounds
1	$(CH_3)_2C=CHCH_3$	4	$(CH_3)_2CHCH_2CH_3$
2	$(CH_3)_2C=CHCH(CH_3)_2$	5	$CH\equiv CCH(CH_3)_2$
3	$CH_3CH=CHCH_2C\equiv CH$	6	$CH\equiv CCH_2CH(CH_3)_2$

Continued of table 9.2

Variant	Compounds	Variant	Compounds
7	$CH_2{=}CHCH(CH_3)_2$	11	$(CH_3)_2C{=}CHC{\equiv}CH$
8	$(CH_3)_2CHCH_2CH_3$	12	$(CH_3)_2CH\ CH_2C{\equiv}CH$
9	$CH{\equiv}CCH(CH_3)_2$	13	$(CH_3)_2C{=}CHCH{=}CH_2$
10	$CH{\equiv}CCH_2CH(CH_3)_2$	14	$CH{\equiv}C(CH_2)_2C(CH_3)_3$

Exercise 3

Write a balanced equation for the complete combustion of a hydrocarbon given in the table 9.3.

Table 9.3 – Variants of the problem

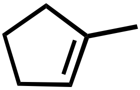
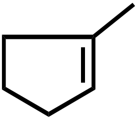
Variant	Hydrocarbon	Variant	Hydrocarbon
1	$CH_3CH{=}CHCH_2CH(CH_3)_2$	8	$CH{\equiv}C(CH_2)_2C(CH_3)_3$
2	$(CH_3)_2C{=}CHCH{=}CH_2$	9	$CH_2{=}CHC(CH_3)_3$
3	$(CH_3)_2CHCH{=}CHCH_3$	10	$(CH_3)_2CH\ CH_2C{\equiv}CH$
4	$CH_3CH{=}CHCH_2CH(CH_3)_2$	11	$(CH_3)_2C{=}CHC{\equiv}CH$
5	$CH_3CH{=}CHCH_2C{\equiv}CH$	12	$CH_2{=}CHCH(CH_3)_2$
6	$(CH_3)_2C{=}CHCH(CH_3)_2$	13	$CH{\equiv}C(CH_2)_2C(CH_3)_3$
7	$(CH_3)_2C{=}CHCH_3$	14	$(CH_3)_2C{=}CH_2$

Exercise 4

- Give the IUPAC name for each of the following unsaturated hydrocarbons (table 9.4);
- Using Markovnikov's rule, predict the predominant product in the HCl addition reaction;

- Write an equation for the complete hydration and hydrogenation.

Table 9.4 – Variants of the problem

Variant	Unsaturated hydrocarbon
1	
2	
3	
4	
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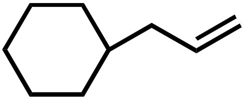
6	
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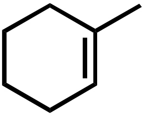
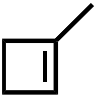
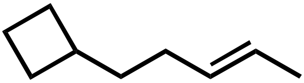
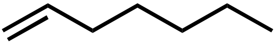
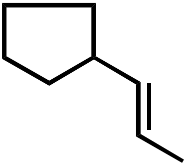
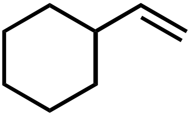
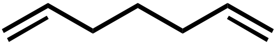
8	
9	
10	
11	

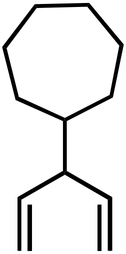
Continued of table 9.4

Variant	Unsaturated hydrocarbon
12	
13	
14	

Exercise 5

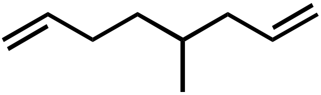
Match the name for each of the following unsaturated hydrocarbons with the formula (table 9.5).

Example:

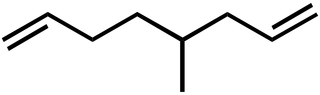
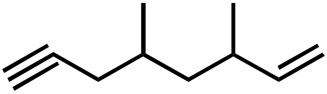
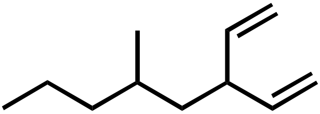
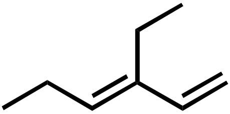
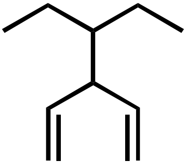
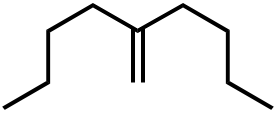
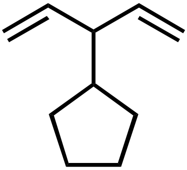


(1-Vinyl-allyl)-cycloheptane

Table 9.5 – Variants of the problem

IUPAC name	Formula
3-Ethyl-hexa-1,3-diene	

Continued of table 9.5

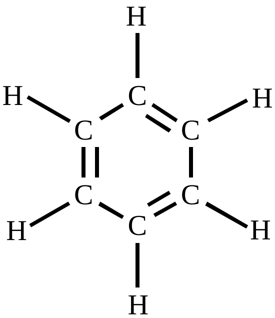
IUPAC name	Formula
3-Ethyl-hexa-1,3-diene	
3-(pentan-3-yl)-pentadiene-1,4	
2-butyhex-1-ene	
4-Methyl-octa-1,7-diene	
(1-Vinyl-allyl)-cyclopentane	
3,5-Dimethyl-oct-1-en-7-yne	
3-(2-methylpentyl)-penta-1,4-diene	

CHAPTER 10 Aromatic hydrocarbons

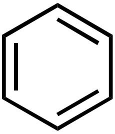
10.1 The main provisions of aromatic hydrocarbons

Aromatic hydrocarbons are the third class of unsaturated hydrocarbons; the alkenes and alkynes (chapter 8, 9) are the other two classes. An aromatic hydrocarbon is an unsaturated cyclic hydrocarbon that does not readily undergo addition reactions. This reaction behavior, which is very different from that of alkenes and alkynes, explains the separate classification for aromatic hydrocarbons.

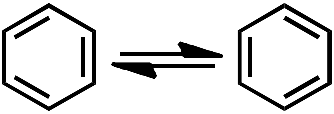
The fact that, even though they are unsaturated compounds, aromatic hydrocarbons don't readily undergo addition reactions suggests that the bonding present in this type of compound must differ significantly from that in alkenes and alkynes. Such is indeed the case. Let's look at the bonding present in benzene, the simplest aromatic hydrocarbon, to explore this new type of bonding situation and to also characterize the aromatic hydrocarbon functional group. Benzene is a symmetrical molecule with a molecular formula of C_6H_6, has a structural formula that is often formalized as that of a cyclohexatriene – in other words, as a structural formula that involves a six-membered carbon ring in which three double bonds are present:



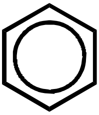
or



The equivalent nature of the carbon–carbon bonds in benzene is addressed by considering the correct bonding structure for benzene to be an average of the two “triene” structures. Related to this “average”-structure situation is the concept that electrons associated with the ring double bonds are not held between specific carbon atoms; instead, they are free to move “around” the carbon ring. Thus the true structure for benzene, an intermediate between that represented by the two “triene” structures, is a situation in which all carbon–carbon bonds are equivalent; they are neither single nor double bonds but something in between. Placing a double-headed arrow between the conventional structures that are averaged to obtain the true structure is one way to denote the average structure:



An alternative notation for denoting the bonding in benzene – a notation that involves a single structure – is:



In this “circle-in-the-ring” structure for benzene, the circle denotes the electrons associated with the double bonds that move “around” the ring. Each carbon atom in the ring can be considered to participate in three conventional (localized) bonds (two C–C bonds and one C–H bond) and in one delocalized bond (the circle) that involves all six carbon atoms. A delocalized bond is a covalent bond in which electrons are shared among more than two atoms. This delocalized bond is what causes benzene and its derivatives to be resistant to addition reactions, a property normally associated with unsaturation in a molecule.

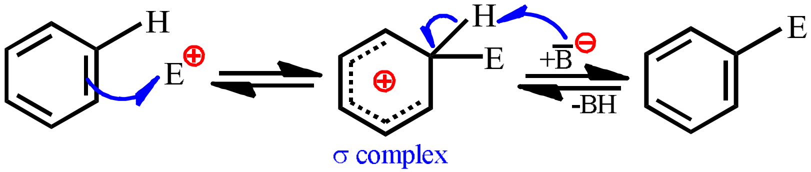
10.2 Physical properties of aromatic hydrocarbons

1. Aromatic hydrocarbons like benzene are colorless and have characteristic odor.
2. Benzene is toxic and carcinogenic in nature.
3. It is a non-polar molecule and exists in the form of colorless liquid and highly inflammable in nature.
4. That is the reason, the bottle of benzene are marketed with the warning of toxic and flammable liquid.
5. Because of the high percentage of carbon atom compare to alkanes, benzene burns with sooty flame and less denser than water.
6. The density of benzene is 0.8765 g/cm^3 and melts at 278.7 K. The boiling point of benzene is 353.3 K temperature.

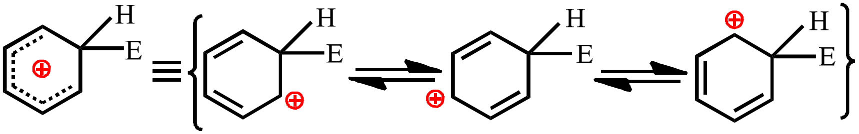
10.3 Chemical reactions of aromatic hydrocarbons

1. Electrophilic substitution reactions. The most common

substitution with benzene is electrophilic substitution reaction which is a multi step reaction. The catalysts and co-reagents react to generate a strong electrophilic species in initial step of the substitution. Electrophile interacts with benzene with to form a cyclohexadienyl cation which is known as Wheland complex or the σ complex or the arenium ion. In second step, base involves in reaction and reacts with σ complex to form substituted product through deprotonation:



Arenium ion is a stable intermediate due to delocalization of positive charge on ring:



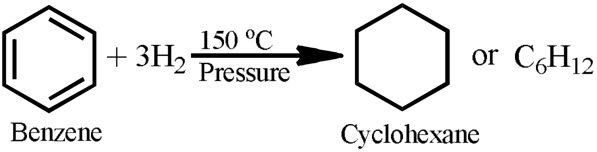
Different electrophilic substitution reactions with electrophile, products and catalyst as follows (table 10.1).

2. Addition reactions of benzene. Benzene shows some of addition reactions like alkene and alkyne under more drastic condition to form additional products. These additional products are more stable and behave as saturated hydrocarbons. The most common addition reactions of benzene are hydrogenation and halogenation results the formation of cyclohexane and benzene hexachloride respectively (reaction 10.1). Hydrogenation of benzene takes place in the presence of catalyst like nickel or

palladium at 475 – 500 K temperature.

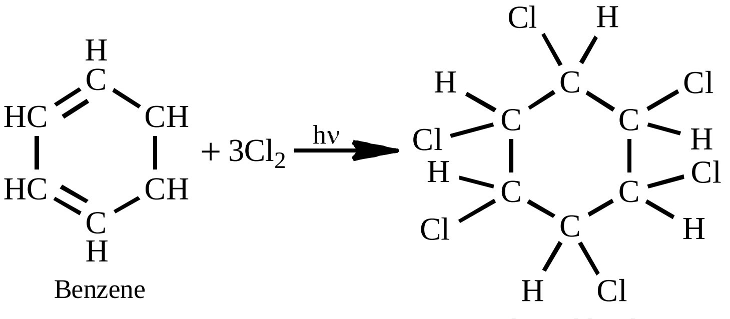
Table 10.1 – Various electrophilic substitution reactions of benzene

Electrophilic substitution reaction	Reaction equation	Electron-phile
Halogenation	$C_6H_6 + Cl_2$ & heat $\rightarrow C_6H_5Cl+HCl$ chlorobenzene	$Cl^{(+)}$ or $Br^{(+)}$
Nitration	$FeCl_3$ catalyst $C_6H_6 + HNO_3$ & heat $\rightarrow C_6H_5NO_2+HCl$ H_2SO_4 catalyst nitrobenzene	$NO_2^{(+)}$
Sulphonation	$C_6H_6 + H_2SO_4+SO_3 \rightarrow C_6H_5SO_3H+H_2O$ & heat benzenesulphonic acid	$SO_3H^{(+)}$
Friedel-crafts alkylation	C_6H_6 + R–Cl & heat $\rightarrow C_6H_5R+HCl$ $AlCl_3$ catalyst an arena	$R^{(+)}$
Friedel-crafts acylation	C_6H_6 + RCOCl & heat$\rightarrow C_6H_5COR+HCl$ $AlCl_3$ catalyst an aryl ketone	$RCO^{(+)}$



(10.1)

In the presence of sunlight, benzene shows additional reaction with halogens like chlorine or bromine to form additional products. For example, with chlorine, it forms benzene hexachloride which is also called as BHC or gamaxine and used as insecticide (reaction 10.2). Since this halogenation takes place in the presence of light without any catalyst, therefore reaction follows free radical mechanism:

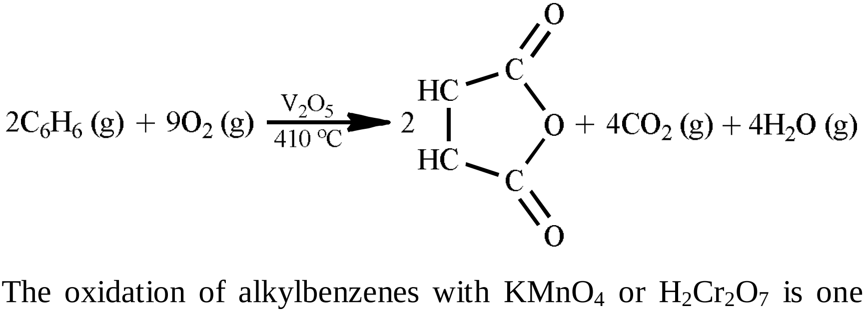


(10.2)

3. Oxidation of benzene. The combustion of benzene forms carbon dioxide and water like other hydrocarbons (reaction 10.3). It burns with sooty flame due to high carbon content compare to other hydrocarbons:

$$2C_6H_6 + 15O_2 \rightarrow 2CO_2 + 6H_2O + \text{heat energy} \qquad (10.3)$$

While the controlled oxidation in the presence of catalyst like vanadium pentaoxide (V_2O_5) at 725 K temperature results maleic anhydride:



The oxidation of alkylbenzenes with $KMnO_4$ or $H_2Cr_2O_7$ is one example of the considerable reactivity found with benzyl radicals (Fig. 10.1). In contrast to non-benzylic alkanes, the oxidation of alkylbenzenes yields benzoic acid. In other words, carbon-carbon single bonds are broken. However, the alkylbenzene must contain at least one benzylic hydrogen atom. Therefore, tert-butylbenzene is not oxidized. In addition, the reaction mixture must be heated for a considerable amount of time in order to obtain complete conversion to benzoic acid.

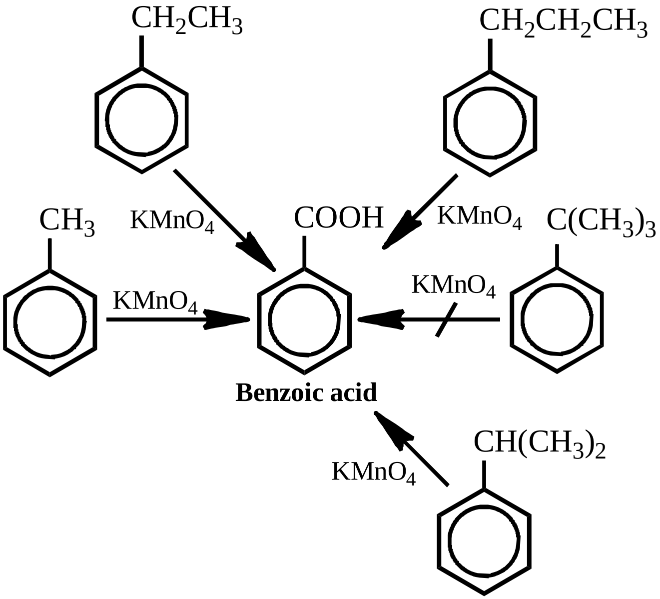


Fig.10.1 – Oxidation of alkyl benzenes

CONCEPTS TO REMEMBER

Aromatic hydrocarbons. Benzene, the simplest aromatic hydrocarbon, and other members of this family of compounds contain a six-membered ring with a cyclic, delocalized bond. This aromatic ring is often drawn as a hexagon containing a circle, which represents six electrons that move freely around the ring.

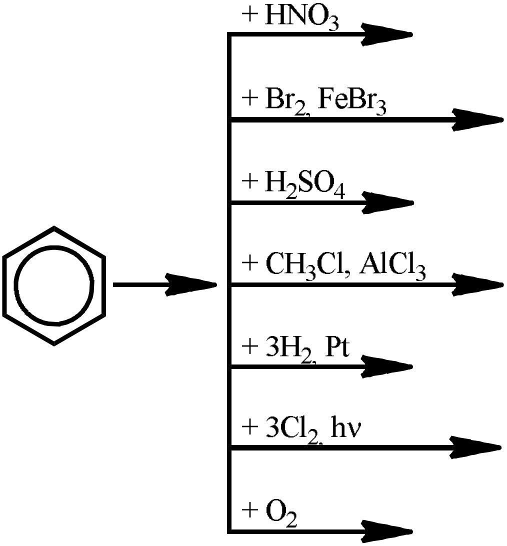
Nomenclature of aromatic hydrocarbons. Monosubstituted benzene compounds are named by adding the substituent name to the word benzene. Positions of substituents in disubstituted benzenes are indicated by using a numbering system or the ortho- (1,2), meta- (1,3) and para- (1,4) prefix system.

Chemical reactions of aromatic hydrocarbons. Aromatic hydrocarbons undergo substitution reactions rather than addition reactions. Important substitution reactions are alkylation and halogenation.

INDIVIDUAL TEST PAPER

Exercise 1

Complete the reactions of benzene with the substances given.



Exercise 2

Write a balanced equation for the reaction between reactants given in the table 10.2.

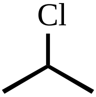
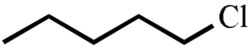
Table 10.2 – Variants of the problem

Variant	Compounds
1	$C_6H_5C_2H_5 + Cl_2$ (UV light)$\rightarrow$
2	$C_6H_5C_3H_7 + HNO_3\rightarrow$
3	$C_6H_5CH_3 + H_2SO_4\rightarrow$
4	$C_6H_5CH_3 + KMnO_4\rightarrow$
5	$C_6\ H_5CH_3 + Cl_2\ (AlCl_3)\rightarrow$
6	$C_6\ H_5CH_3 + O_2 \rightarrow$
7	$C_6\ H_5CH_3 + Cl_2$ (UV light)$\rightarrow$
8	$C_6H_5CH_3 + HNO_3\rightarrow$
9	$C_6H_5C_4H_9 + H_2SO_4\rightarrow$
10	$C_6H_5C_3H_7 + KMnO_4\rightarrow$
11	$C_6\ H_5C_2H_5 + Cl_2\ (AlCl_3)\rightarrow$
12	$C_6\ H_5C_4H_9 + O_2 \rightarrow$

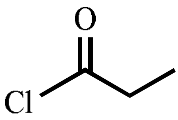
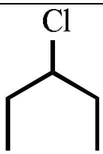
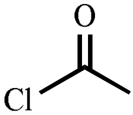
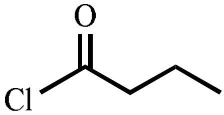
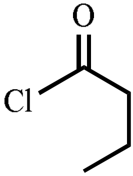
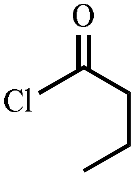
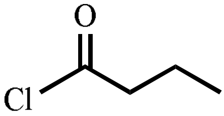
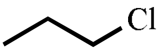
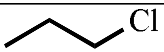
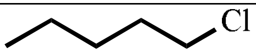
Exercise 3

Write an equation for the Friedel-crafts reaction between benzene and reactant given in the table 10.3.

Table 10.3 – Variants of the problem

Variant	Compounds	Variant	Compounds
1		2	

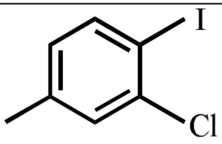
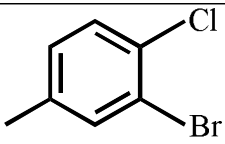
Continued of table 10.3

Variant	Compounds	Variant	Compounds
3		8	
4		9	
5		10	
6		11	
7		12	

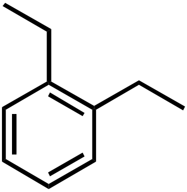
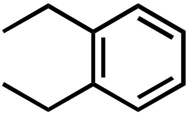
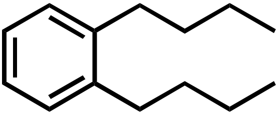
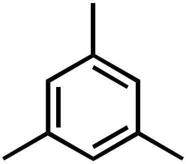
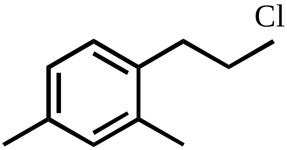
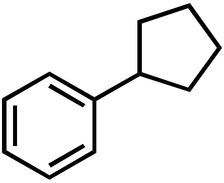
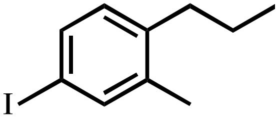
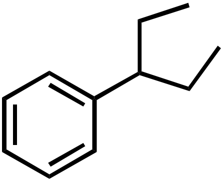
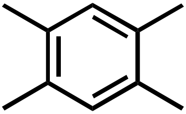
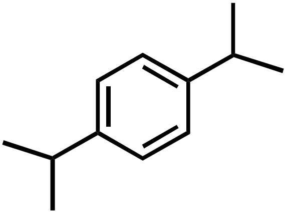
Exercise 4

Give the IUPAC name for each of the following compounds (table 10.4).

Table 10.4 – Variants of the problem

Variant	Compounds	Variant	Compounds
1		2	

Continued of table 10.4

Variant	Compounds	Variant	Compounds
3		8	
4		9	
5		10	
6		11	
7		12	

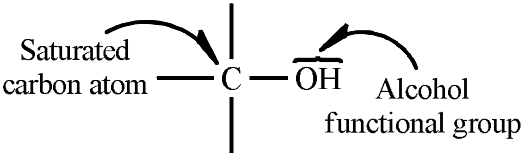
CHAPTER 11

Derivatives hydrocarbons: Alcohols, Ethers and Phenols

11.1 The main provisions of hydrocarbon derivatives

We begin our discussion of hydrocarbon derivatives containing a single oxygen atom by considering alcohols, substances with the generalized formula **R–OH**.

An alcohol is an organic compound in which an –OH group is bonded to a saturated carbon atom. ***A saturated carbon atom*** is a carbon atom that is bonded to four other atoms:



The –OH group, the functional group that is characteristic of an alcohol, is called a ***hydroxyl group***. A hydroxyl group is the –OH functional group.

Examples of structural formulas for alcohols include:

$CH_3 - OH$ Methanol

$CH_3 - CH_2 - OH$ Ethanol

$CH_3 - CH_2 - CH_2 - OH$ Propanol

Alcohols may be viewed structurally as being alkyl derivatives of water in which a hydrogen atom has been replaced by an alkyl group:

$$H-\underset{\cdot\cdot}{\ddot{O}}-H \qquad\qquad R-\underset{\cdot\cdot}{\ddot{O}}-H$$

Water An alcohol

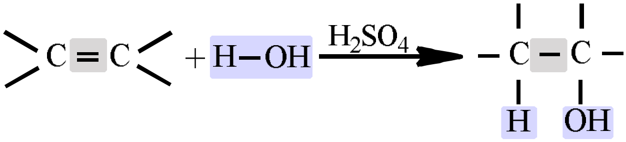
Alcohols may also be viewed structurally as hydroxyl derivatives of alkanes in which a hydrogen atom has been replaced by a hydroxyl group:

$$R-H \qquad\qquad R-OH$$

An alkane An alcohol

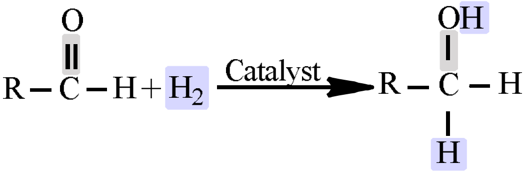
11.2 Preparation of alcohols

Alkenes react with water (an unsymmetrical addition agent) in the presence of sulfuric acid (the catalyst) to form an alcohol (reaction 11.1). Markovnikov's rule is used to determine the predominant alcohol product.

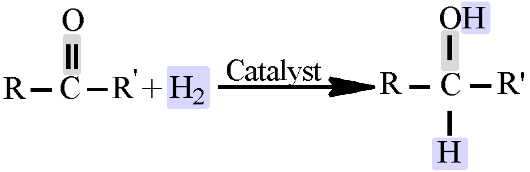


$$>C=C< + H-OH \xrightarrow{H_2SO_4} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}- \tag{11.1}$$

Another method of synthesizing alcohols involves the addition of H_2 to a carbon–oxygen double bond (a carbonyl group). ***A carbonyl group*** behaves very much like a carbon–carbon double bond when it reacts with H_2 under the proper conditions (reaction 11.2, 11.3).



$$R-\overset{\overset{O}{\|}}{C}-H + H_2 \xrightarrow{Catalyst} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H \tag{11.2}$$

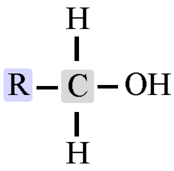


$$R-\overset{\overset{O}{\|}}{C}-R' + H_2 \xrightarrow{\text{Catalyst}} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-R' \qquad (11.3)$$

As a result of H_2 addition, the oxygen of the carbonyl group is converted to an –OH group.

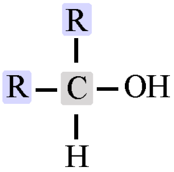
11.3 Classification of alcohols

Alcohols are classified as ***primary*** (1°), ***secondary*** (2°), or ***tertiary*** (3°) depending on the number of carbon atoms bonded to the carbon atom that bears the hydroxyl group. A primary alcohol is an alcohol in which the hydroxyl-bearing carbon atom is bonded to only one other carbon atom. A secondary alcohol is an alcohol in which the hydroxyl-bearing carbon atom is bonded to two other carbon atoms. A tertiary alcohol is an alcohol in which the hydroxyl-bearing carbon atom is bonded to three other carbon atoms. Chemical reactions of alcohols often depend on alcohol class (1°, 2°, or 3°):



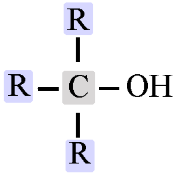
$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH$$

1° alcohol



$$R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH$$

2° alcohol



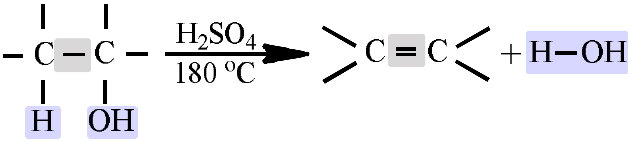
$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH$$

3° alcohol

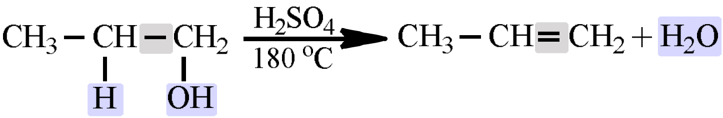
11.4 Chemical reactions of alcohols

Of the many chemical reactions that alcohols undergo, we consider four in this section: intramolecular and intermolecular dehydration, oxidation and halogenation.

1. Intramolecular Alcohol Dehydration. A dehydration reaction is a chemical reaction in which the components of water (H and OH) are removed from a single reactant or from two reactants (H from one and OH from the other). In intramolecular dehydration, both water components are removed from the same molecule. Reaction conditions for the intramolecular dehydration of an alcohol are a temperature of 180 °C and the presence of sulfuric acid (H_2SO_4) as a catalyst. The dehydration product is an alkene (reaction 11.4, 11.5).



(11.4)



$$CH_3-\underset{\overset{|}{H}}{CH}-\underset{\overset{|}{OH}}{CH_2} \xrightarrow[180\ ^{\circ}C]{H_2SO_4} CH_3-CH=CH_2+H_2O \qquad (11.5)$$

Dehydration of an alcohol can result in the production of more than one alkene product. This happens when there is more than one neighboring carbon atom from which hydrogen loss can occur. Dehydration of 2-butanol is produces two alkenes (Fig. 11.1).

The dominant product can be predicted using Zaitsev's rule, named after the Russian chemist Alexander Zaitsev. ***Zaitsev's rule*** states that the major product in an intramolecular alcohol dehydration reaction is the alkene that has the greatest number of alkyl groups attached to the carbon atoms of the double bond. In the preceding reaction (Fig. 1.1), 2-butene (with two alkyl groups) is favored over 1-butene (with one alkyl group).

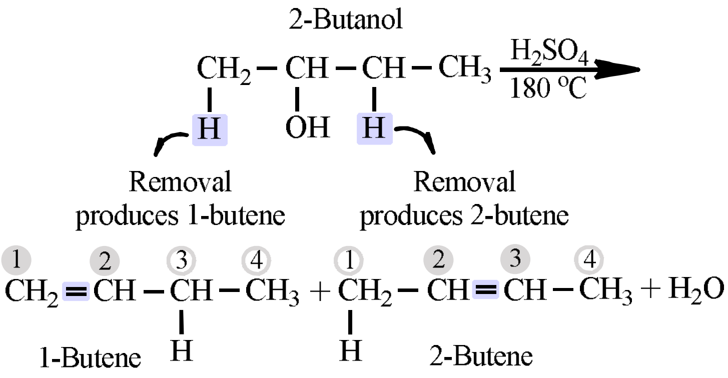
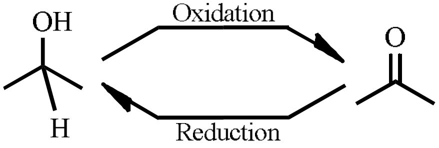


Fig. 11.1 – 2-Butanol dehydradation

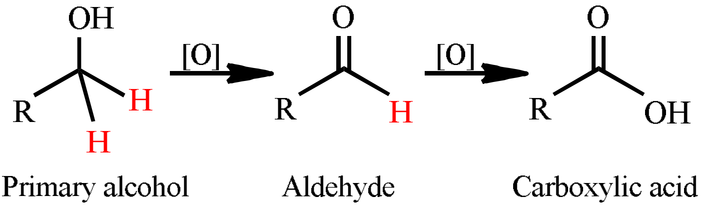
2. Intermolecular Alcohol Dehydration. At a lower temperature (140 °C) than that required for alkene formation (180 °C), an intermolecular rather than an intramolecular alcohol dehydration process can occur to produce an ether – a compound with the general structure R–O–R. In such ether formation, two alcohol molecules interact, an H atom being lost from one and an –OH group from the other. The resulting “leftover” portions of the two alcohol molecules join to form the ether. This reaction (11.6), which gives useful yields only for primary alcohol reactants (2 and 3 alcohols yield predominantly alkenes), can be written as:

$$R-O-H+H-O-R \longrightarrow R-O-R+H_2O \qquad (11.6)$$

3. Oxidation. In this section, we will explore the reverse process, called oxidation, which involves an increase in oxidation state:



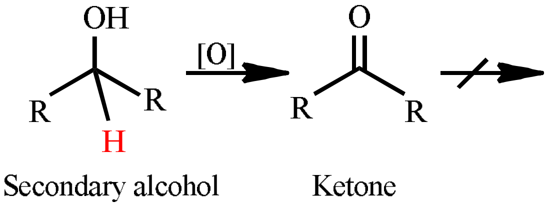
The outcome of an oxidation process depends on whether the starting alcohol is primary, secondary or tertiary (reaction 11.7). Let’s first consider the oxidation of a primary alcohol:



(11.7)

Notice that a primary alcohol has two protons at the α position (the carbon atom bearing the hydroxyl group). As a result, primary alcohols can be oxidized twice. The first oxidation produces an aldehyde, and then oxidation of the aldehyde produces a carboxylic acid (reaction 11.7).

Secondary alcohols only have one proton at the α position so they can only be oxidized once (reaction 11.8), forming a ketone:

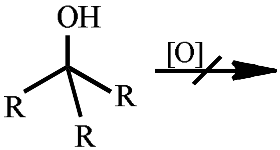


(11.8)

Generally speaking, the ketone is not further oxidized. Tertiary alcohols do not have any protons at the α position, and as a result, they generally do not undergo oxidation (reaction 11.9). A number of different oxidizing agents can be used for the oxidation, including potassium permanganate ($KMnO_4$), potassium dichromate ($K_2Cr_2O_7$), and chromic acid (H_2CrO_4).

4. Halogenation. Alcohols undergo halogenation reactions in which a halogen atom is substituted for the hydroxyl group,

producing an alkyl halide. Alkyl halide production in this manner is superior to alkyl halide production through halogenation of an alkane because mixtures of products are not obtained. A single product is produced in which the halogen atom is found only where the −OH group was originally located.



Tertiary alcohol

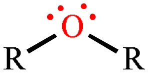
(11.9)

Several different halogen-containing reactants, including phosphorus trihalides (PX_3; X is Cl or Br), are useful in producing alkyl halides from alcohols:

$$3R-OH+PX_3 \xrightarrow{\text{Heat}} 3R-X+H_3PO_3 \qquad (11.10)$$

11.5 Ethers. Preparation of ethers

Ethers are compounds that exhibit an oxygen atom bonded to two R groups, where each R group can be an alkyl, aryl, or vinyl group:



1. Industrial preparation of diethyl ether. Diethyl ether is prepared industrially via the acid-catalyzed dehydration of ethanol. (Fig. 11.2) The mechanism of this process is believed to involve an S_N2 process. This process has many limitations. For example, it only works well for primary alcohols (since it proceeds via an S_N2 pathway), and it produces symmetrical ethers. As a result, this

process for preparing ethers is too limited to be of any practical value for organic synthesis.

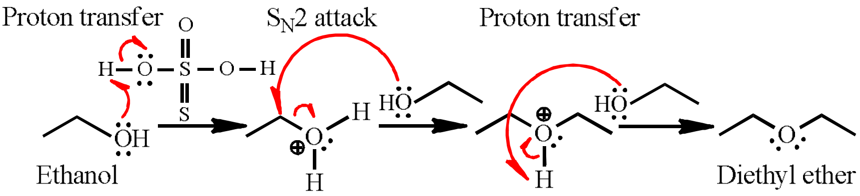


Fig. 11.2 – Industrial preparation of diethyl ether

2. Williamson ether synthesis. Ethers can be readily prepared via a two-step process called a Williamson ether synthesis. In the first step, the alcohol is deprotonated to form an alkoxide ion. In the second step, the alkoxide ion functions as a nucleophile in an S_N2 reaction.

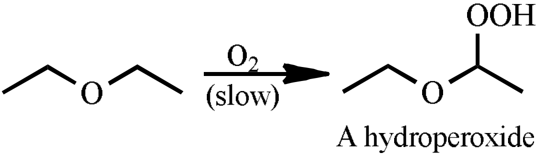
11.6 Reactions of ethers

Ethers are generally unreactive under basic or mildly acidic conditions. As a result, they are an ideal choice as solvents for many reactions. Nevertheless, ethers are not completely unreactive, and two reactions of ethers will be explored in this section.

1. Acidic cleavage. When heated with a concentrated solution of a strong acid, ether will undergo acidic cleavage, in which the ether is converted into two alkyl halides:

$$R-O-R \xrightarrow[\text{Heat}]{\text{Excess HX}} R-X+R-X+H_2O \qquad (11.11)$$

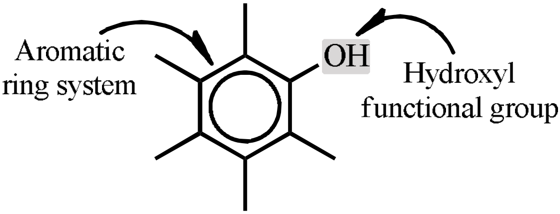
2. Autooxidation. Ethers undergo autooxidation in the presence of atmospheric oxygen to form hydroperoxides:



(11.12)

11.7 Phenols

A phenol is an organic compound in which an –OH group is attached to a carbon atom that is part of an aromatic carbon ring system:



The general formula for phenols is Ar–OH, where Ar represents an aryl group. An aryl group is an aromatic carbon ring system from which one hydrogen atom has been removed. A hydroxyl group is thus the functional group for both phenols and alcohols. The reaction chemistry for phenols is sufficiently different from that for nonaromatic alcohols to justify discussing these compounds separately. Remember that phenols contain a "benzene ring" and that the chemistry of benzene is much different from that of other unsaturated hydrocarbons.

11.8 Physical and chemical properties of phenols

Phenols are generally low-melting solids or oily liquids at room temperature. Most of them are only slightly soluble in water. Many phenols have antiseptic and disinfectant properties. The simplest phenol, phenol itself, is a colorless solid with a medicinal odor. Its melting point is 41 ºC, and it is more soluble in water than are most other phenols.

We have previously noted that the chemical properties of phenols are significantly different from those of alcohols. The similarities and differences between these two reaction chemistries are as follows:

1. Both alcohols and phenols are flammable.

2. Dehydration is a reaction of alcohols but not of phenols; phenols cannot be dehydrated.

3. Both 1º and 2º alcohols are oxidized by mild oxidizing agents. Tertiary (3º) alcohols and phenols do not react with the oxidizing agents that cause 1º and 2º alcohol oxidation. Phenols can be oxidized by stronger oxidizing agents.

4. Both alcohols and phenols undergo halogenation in which the hydroxyl group is replaced by a halogen atom in a substitution reaction.

CONCEPTS TO REMEMBER

Alcohols. Alcohols are organic compounds that contain an –OH group attached to a saturated carbon atom. The general formula for an alcohol is R–OH, where R is an alkyl group.

Nomenclature of alcohols. The IUPAC names of simple alcohols end in ***-ol***, and their carbon chains are numbered to give precedence to the location of the –OH group. Alcohol common names contain the word alcohol preceded by the name of the alkyl group.

Isomerism for alcohols. Constitutional isomerism is possible for alcohols containing three or more carbon atoms. Both skeletal and positional isomers are possible.

Physical properties of alcohols. Alcohol is molecules hydrogen-bond to each other and to water molecules. They thus have higher-than-normal boiling points, and the low-molecular-mass alcohols are soluble in water.

Classification of alcohols. Alcohols are classified on the basis of the number of carbon atoms bonded to the carbon attached to the –OH group. In primary alcohols, the –OH group is bonded to a carbon atom bonded to only one other C atom. In secondary alcohols, the –OH-containing C atom is attached to two other C atoms. In tertiary alcohols, it is attached to three other C atoms.

Alcohol dehydration. Alcohols can be dehydrated in the presence of sulfuric acid to form alkenes or ethers. At 180 ºC, an alkene is produced; at 140 ºC, primary alcohols produce an ether.

Alcohol oxidation. Oxidation of primary alcohols first produces an aldehyde, which is then further oxidized to a carboxylic acid. Secondary alcohols are oxidized to ketones, and tertiary alcohols are resistant to oxidation.

Phenols. Phenols have the general formula Ar–OH, where Ar represents an aryl group derived from an aromatic compound. Phenols are named as derivatives of the parent compound phenol, using the conventions for aromatic hydrocarbon nomenclature.

Properties of phenols. Phenols are generally low-melting solids; most are only slightly soluble in water. The chemical reactions of phenols are significantly different from those of alcohols, even though both types of compounds possess hydroxyl groups. Phenols are more resistant to oxidation and do not undergo dehydration. Phenols have acidic properties, whereas alcohols do not.

INDIVIDUAL TEST PAPER

Exercise 1

Name the following alcohols, utilizing IUPAC nomenclature rules (table 11.1).

Table 11.1 – Variants of the problem

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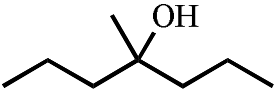
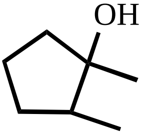
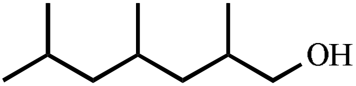
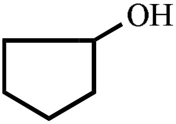
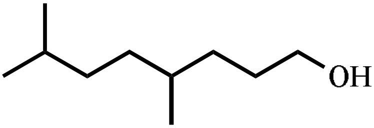
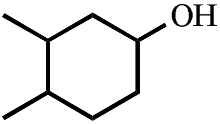
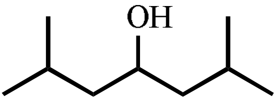
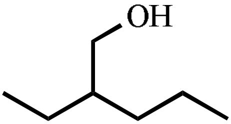
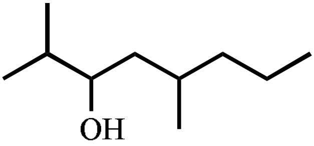
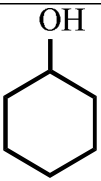
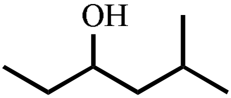
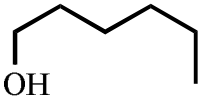
1		7	
2		8	
3		9	
4		10	
5		11	
6		12	

Exercise 2

Classify each of the following alcohols as a primary, secondary or tertiary alcohol (table 11.2).

Table 11.2 – Variants of the problem

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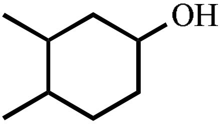
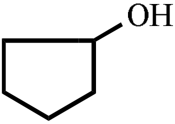
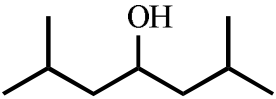
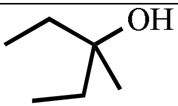
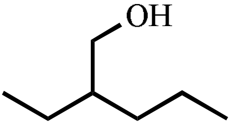
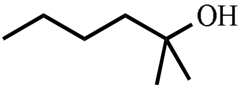
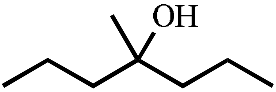
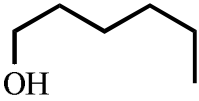
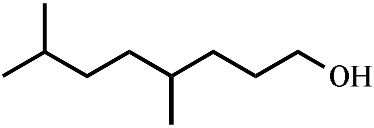
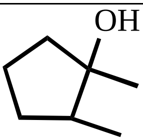
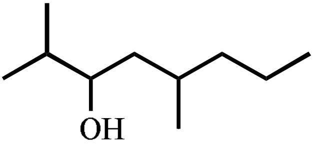
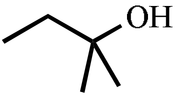
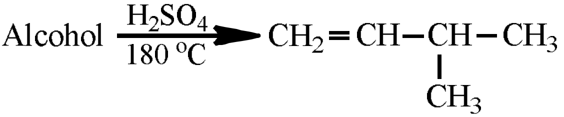
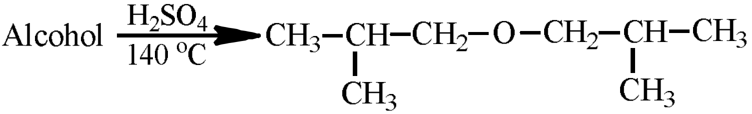
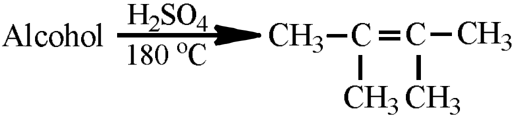
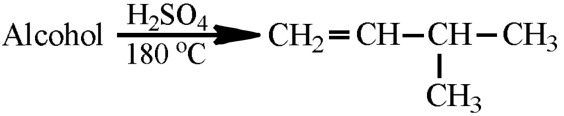
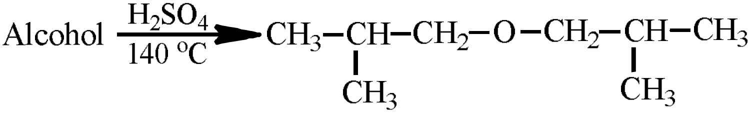
1		7	
2		8	
3		9	
4		10	
5		11	
6		12	

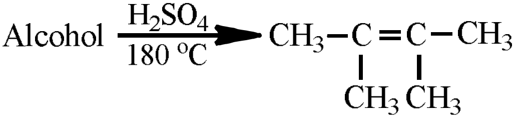
Exercise 3

Identify the alcohol reactant needed to produce each of the following compounds as the major product of an alcohol dehydration reaction (table 11.3).

Table 11.3 – Variants of the problem

Variant	Reactions
1	Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_3-CH=CH-CH_3$
2	 Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_2=CH-\underset{\mid \atop CH_3}{CH}-CH_3$
3	 Alcohol $\xrightarrow[140\ ^{o}C]{H_2SO_4} CH_3-\underset{\mid \atop CH_3}{CH}-CH_2-O-CH_2-\underset{\mid \atop CH_3}{CH}-CH_3$
4	Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_2=CH-CH_2-CH_3$
5	 Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_3-\underset{\mid \atop CH_3}{C}=\underset{\mid \atop CH_3}{C}-CH_3$
6	Alcohol $\xrightarrow[140\ ^{o}C]{H_2SO_4} CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$
7	Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_3-CH=CH-CH_3$
8	 Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_2=CH-\underset{\mid \atop CH_3}{CH}-CH_3$
9	 Alcohol $\xrightarrow[140\ ^{o}C]{H_2SO_4} CH_3-\underset{\mid \atop CH_3}{CH}-CH_2-O-CH_2-\underset{\mid \atop CH_3}{CH}-CH_3$
10	Alcohol $\xrightarrow[180\ ^{o}C]{H_2SO_4} CH_2=CH-CH_2-CH_3$

Continued of table 11.3

Variant	Reactions
11	 $\text{Alcohol}\xrightarrow[180\ ^{\circ}C]{H_2SO_4}CH_3-\underset{\underset{CH_3}{\vert}}{C}=\underset{\underset{CH_3}{\vert}}{C}-CH_3$
12	$\text{Alcohol}\xrightarrow[140\ ^{\circ}C]{H_2SO_4}CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$

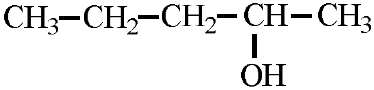
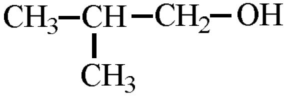
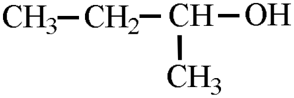
Exercise 4

Draw the structural formula(s) for the product(s) formed by oxidation of the following alcohols with a mild oxidizing agent. If no reaction occurs, write "no reaction" (table 11.4).

Exercise 5

Name the following ethers utilizing IUPAC nomenclature rules (table 11.5).

Table 11.4 – Variants of the problem

Variant	Reactions
1	 $CH_3-CH_2-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_3$
2	 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-OH$
3	 $CH_3-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-OH$

Continued of table 11.4

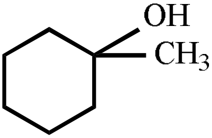
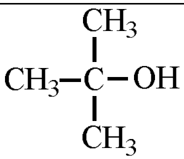
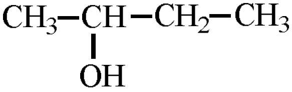
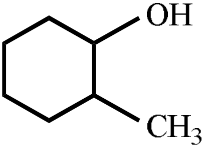
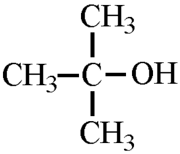
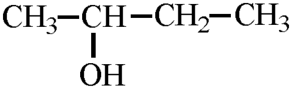
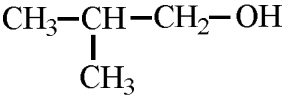
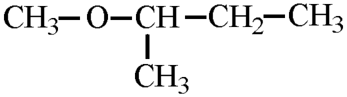
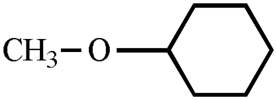
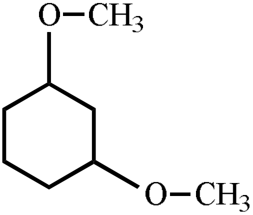
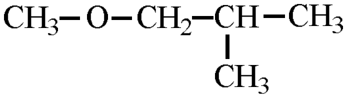
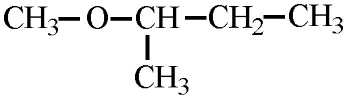
Variant	Reactions
4	
5	$CH_3-CH_2-CH_2-OH$
6	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-OH$
7	 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_2-CH_3$
8	
9	$CH_3-CH_2-CH_2-OH$
10	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-OH$
11	 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_2-CH_3$
12	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-OH$

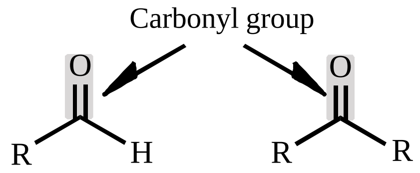
Table 11.5 – Variants of the problem

Variant	Reactions
1	$CH_3-CH_2-O-CH_2-CH_2-CH_3$
2	 $CH_3-O-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$
3	Ethyl methyl ether
4	
5	Dimethyl ether
6	
7	Ethyl propyl ether
8	$CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$
9	 $CH_3-O-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$
10	Propyl buthyl ether
11	$CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$
12	 $CH_3-O-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$

CHAPTER 12 Aldehydes and ketones

12.1 The main provisions of aldehydes and ketones

Aldehydes (RCHO) and ***ketones*** (R_2CO) are similar in structure in that both classes of compounds possess a C=O bond, called a carbonyl group:

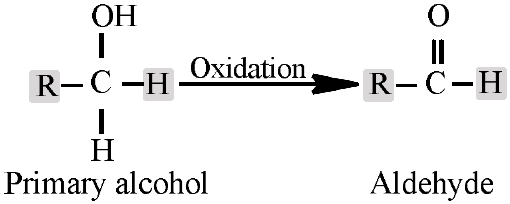


An aldehyde A ketone

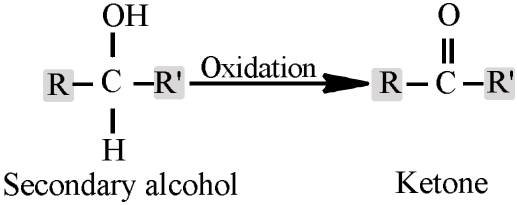
The carbonyl group of an aldehyde is flanked by a hydrogen atom, while the carbonyl group of a ketone is flanked by two carbon atoms.

12.2 Preparation of aldehydes and ketones

When treated with a strong oxidizing agent, primary alcohols are oxidized to carboxylic acids (reaction 12.1). Formation of an aldehyde requires an oxidizing agent, such as PCC, that will not further oxidize the resulting aldehyde. Ketones do not undergo the further oxidation (reaction 12.2), that aldehydes do:

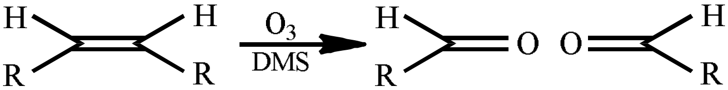


$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \xrightarrow{\text{Oxidation}} R-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad (12.1)$$

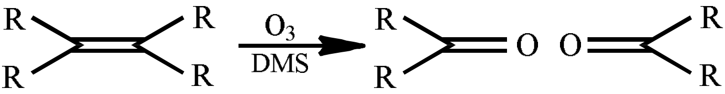


$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-R' \xrightarrow{\text{Oxidation}} R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \qquad (12.2)$$

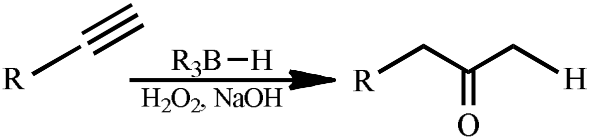
<u>1. Ozonolysis of alkenes.</u> Ozonolysis will cleave a C=C double bond. If either carbon atom bears a hydrogen atom, an aldehyde will be formed:



Tetrasubstituted alkenes are cleaved to form ketones:

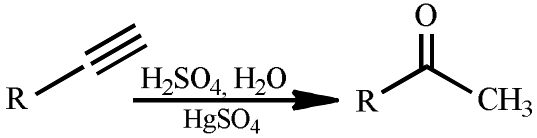


<u>2. Hydroboration-oxidation of terminal alkynes.</u> Hydroboration-oxidation results in an anti-Markovnikov addition of water across the *p* bond, followed by tautomerization of the resulting enol to form an aldehyde:

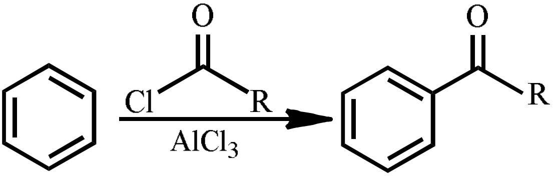


<u>3. Acid-catalyzed hydration of terminal alkynes.</u> This

procedure results in a Markovnikov addition of water across the *p* bond, followed by tautomerization to form a methyl ketone:

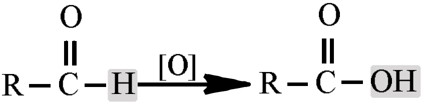


4. Friedel-crafts acylation. Aromatic rings that are not too strongly deactivated will react with an acid halide in the presence of a Lewis acid to produce an aryl ketone:

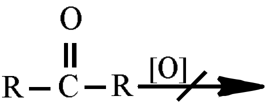


12.3 Reactions of aldehydes and ketones

1. Oxidation of aldehydes and ketones. Aldehydes readily undergo oxidation to carboxylic acids (reaction 12.3), and ketones are resistant to oxidation (reaction 12.4):



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{[O]} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad (12.3)$$

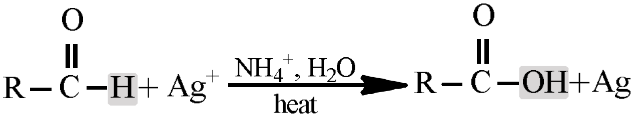


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R \not\xrightarrow{[O]} \qquad (12.4)$$

Because both aldehydes and ketones contain carbonyl groups, we might expect similar oxidation reactions for the two types of compounds. Oxidation of an aldehyde involves breaking a carbon–hydrogen bond, and oxidation of a ketone involves breaking a carbon–carbon bond. The former is much easier to accomplish than the latter. For ketones to be oxidized, strenuous reaction conditions must be employed.

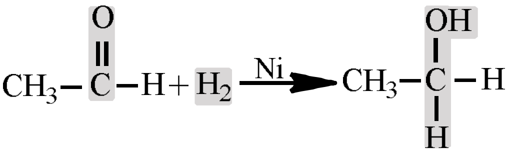
Several tests, based on the ease with which aldehydes are oxidized, have been developed for distinguishing between aldehydes and ketones, for detecting the presence of aldehyde groups in sugars (carbohydrates), and for measuring the amounts of sugars present in a solution.

The Tollens test, also called the silver mirror test, involves a solution that contains silver nitrate ($AgNO_3$) and ammonia (NH_3) in water. When Tollens solution is added to an aldehyde, Ag-ion (the oxidizing agent) is reduced to silver metal, which deposits on the inside of the test tube, forming a silver mirror (reaction 12.5). The appearance of this silver mirror is a positive test for the presence of the aldehyde group:

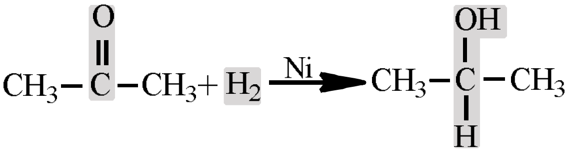


$$R-\overset{O}{\overset{\|}{C}}-H + Ag^+ \xrightarrow[\text{heat}]{NH_4^+,\ H_2O} R-\overset{O}{\overset{\|}{C}}-OH + Ag \qquad (12.5)$$

2. Reduction of aldehydes and ketones. Aldehydes and ketones are easily reduced by hydrogen gas (H_2), in the presence of a catalyst (Ni, Pt, or Cu), to form alcohols:



$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Ni} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H \qquad (12.6)$$



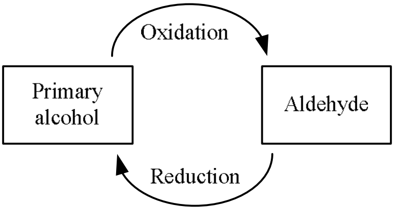
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2 \xrightarrow{Ni} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3 \qquad (12.7)$$

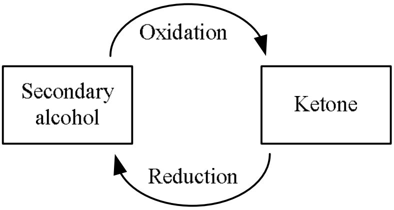
The reduction of aldehydes produces primary alcohols, and the reduction of ketones yields secondary alcohols:

$$\text{Aldehyde} \xrightarrow{\text{Oxidation}} \text{Primary alcohol}$$

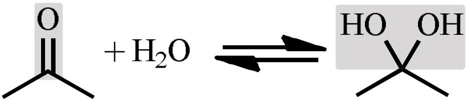
$$\text{Ketone} \xrightarrow{\text{Oxidation}} \text{Secondary alcohol}$$

Aldehyde reduction and ketone reduction to produce alcohols are the “opposite” of the oxidation of alcohols to produce aldehydes and ketones. These “opposite” relationships can be diagrammed as follows:





3. Nucleophilic addition reactions. Hydrate formation. When an aldehyde or ketone is treated with water, the carbonyl group can be converted into a hydrate:



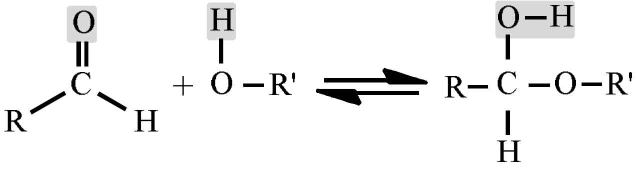
(12.8)

The position of equilibrium generally favors the carbonyl group rather than the hydrate, except in the case of very simple aldehydes, such as formaldehyde.

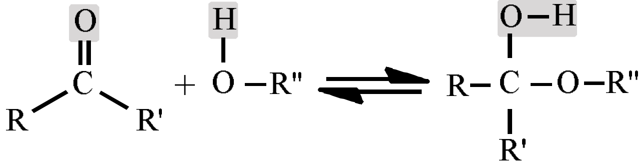
The rate of reaction is relatively slow under neutral conditions but is readily enhanced in the presence of either acid or base. That is, the reaction can be either acid catalyzed or base catalyzed, allowing the equilibrium to be achieved much more rapidly.

4. Reactions with alcohols. Aldehydes and ketones react with alcohols to form hemiacetals and acetals. Reaction with one molecule of alcohol produces a hemiacetal, which is then converted to an acetal by reaction with a second alcohol molecule.

Hemiacetal formation is an addition reaction (12.9, 12.10) in which a molecule of alcohol adds to the carbonyl group of an aldehyde or ketone. The H portion of the alcohol adds to the carbonyl oxygen atom, and the R–O portion of the alcohol adds to the carbonyl carbon atom:

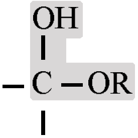


(12.9)



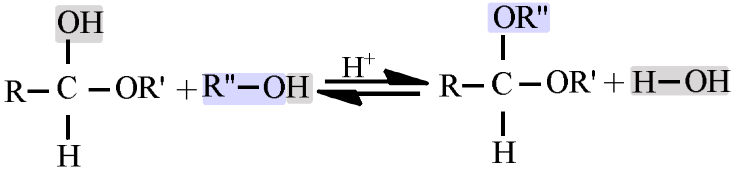
(12.10)

Formally defined, ***a hemiacetal*** is an organic compound in which a carbon atom is bonded to both a hydroxyl group (–OH) and an alkoxy group (–OR). The functional group for a hemiacetal is thus:



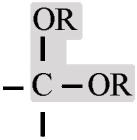
$$-\overset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-OR$$

If a small amount of acid catalyst is added to a hemiacetal reaction mixture, the hemiacetal reacts with a second alcohol molecule, in a condensation reaction, to form an acetal:



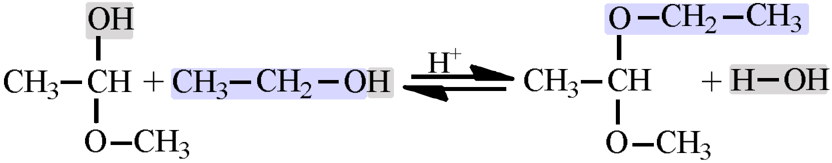
$$R-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-OR' + R''-OH \xrightleftharpoons{H^+} R-\overset{\displaystyle OR''}{\underset{\displaystyle H}{C}}-OR' + H-OH$$

An acetal is an organic compound in which a carbon atom is bonded to two alkoxy groups (–OR). The functional group for an acetal is thus:



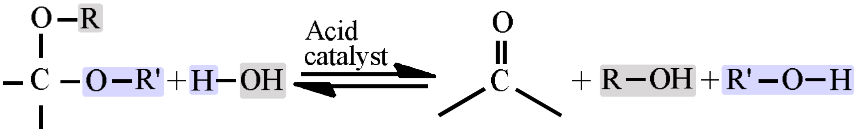
$$-\overset{\displaystyle OR}{\underset{|}{C}}-OR$$

A specific example of acetal formation from a hemiacetal is:

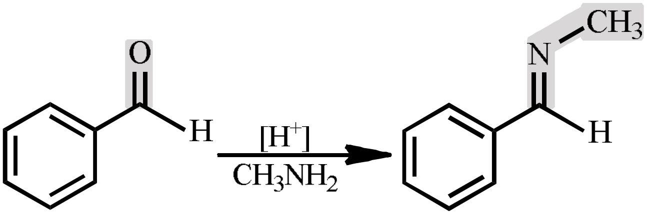


$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle O-CH_3}{CH}} + CH_3-CH_2-OH \xrightleftharpoons{H^+} CH_3-\overset{\displaystyle O-CH_2-CH_3}{\underset{\displaystyle O-CH_3}{CH}} + H-OH$$

Acetals, unlike hemiacetals, are easily isolated from reaction mixtures. They are stable in basic solution but undergo hydrolysis in acidic solution. A hydrolysis reaction is the reaction of a compound with H_2O, in which the compound splits into two or more fragments as the elements of water (H– and –OH) are added to the compound. The products of acetal hydrolysis are the aldehyde or ketone and alcohols that originally reacted to form the acetal:

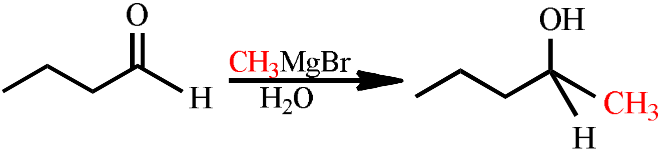


5. Reaction with primary amines. In mildly acidic conditions, an aldehyde or ketone will react with a primary amine to form an amine:



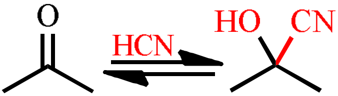
(12.11)

6. Reaction with grignard reagents. When treated with a Grignard reagent, aldehydes and ketones are converted into alcohols, accompanied by the formation of a new C–C bond:



(12.12)

7. Cyanohydrin formation. When treated with hydrogen cyanide (HCN), aldehydes and ketones are converted into cyanohydrins, which are characterized by the presence of a cyano group and a hydroxyl group connected to the same carbon atom:



(12.13)

This reaction was found to occur more rapidly in mildly basic conditions. In the presence of a catalytic amount of base, a small amount of hydrogen cyanide is deprotonated to give cyanide ions, which catalyze the reaction.

CONCEPTS TO REMEMBER

The carbonyl group. A carbonyl group consists of a carbon atom bonded to an oxygen atom through a double bond. Aldehydes and ketones are compounds that contain a carbonyl functional group. The carbonyl carbon in an aldehyde has at least one hydrogen attached to it, and the carbonyl carbon in a ketone has no hydrogens attached to it.

Nomenclature of aldehydes and ketones. The IUPAC names of aldehydes and ketones are based on the longest carbon chain that contains the carbonyl group. The chain numbering is done from the end that results in the lowest number for the carbonyl group. The names of aldehydes end in ***-al***, those of ketones in ***-one***.

Isomerism for aldehydes and ketones. Constitutional isomerism is possible for aldehydes and for ketones when four or more carbon atoms are present. Aldehydes and ketones with the same number of carbon atoms and the same degree of saturation have the same molecular formula and thus are functional group isomers of each other.

Physical properties of aldehydes and ketones. The boiling points of aldehydes and ketones are intermediate between those of alcohols and alkanes. The polarity of the carbonyl groups enables aldehyde and ketone molecules to interact with each other through dipole–dipole interactions. They cannot, however, hydrogen-bond to each other. Lower-molecular-mass aldehydes and ketones are soluble in water.

Preparation of aldehydes and ketones. Oxidation of primary and secondary alcohols, using mild oxidizing agents, produces aldehydes and ketones, respectively.

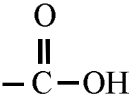
Oxidation and reduction of aldehydes and ketones. Aldehydes are easily oxidized to carboxylic acids; ketones do not readily undergo oxidation. Reduction of aldehydes and ketones produces primary and secondary alcohols, respectively.

Hemiacetals and acetals. A characteristic reaction of aldehydes and ketones is the addition of an alcohol across the carbonyl double bond to produce hemiacetals. The reaction of a second alcohol molecule with a hemiacetal produces an acetal.

CHAPTER 13 Carboxylic acids and derivatives. Amines

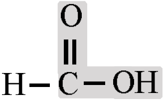
13.1 Carboxylic acids

A carboxylic acid is an organic compound whose functional group is the carboxyl group. A carboxyl group is a carbonyl group (C=O) with a hydroxyl group (–OH) bonded to the carbonyl carbon atom. A general structural representation for a carboxyl group is:



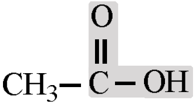
$$-\overset{\underset{\|}{O}}{C}-OH$$

The simplest carboxylic acid has a hydrogen atom attached to the carboxyl group carbon atom:

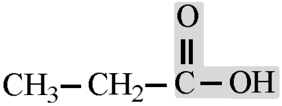


$$H-\overset{\underset{\|}{O}}{C}-OH$$

Structures for the next two simplest carboxylic acids, those with methyl and ethyl alkyl groups, are:

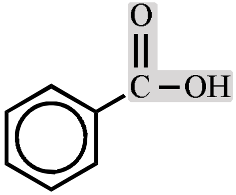


$$CH_3-\overset{\underset{\|}{O}}{C}-OH$$

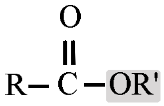


$$CH_3-CH_2-\overset{\underset{\|}{O}}{C}-OH$$

The structure of the simplest aromatic carboxylic acid involves a benzene ring to which a carboxyl group is attached:

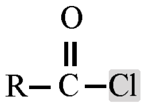


A carboxylic acid derivative is an organic compound that can be synthesized from or converted into a carboxylic acid. Four important families of carboxylic acid derivatives are esters, acid chlorides, acid anhydrides, and amides. The group attached to the carbonyl carbon atom distinguishes these derivative types from each other and also from carboxylic acids:



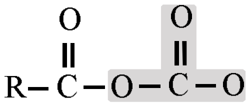
$R-\overset{\overset{O}{\|}}{C}-OR'$

Ester



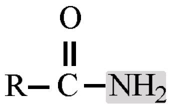
$R-\overset{\overset{O}{\|}}{C}-Cl$

Acid chloride



$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O$

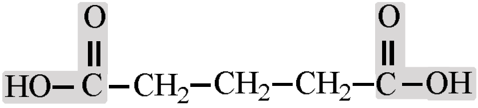
Acid anhydride



$R-\overset{\overset{O}{\|}}{C}-NH_2$

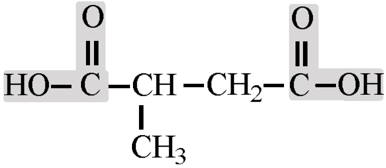
Amide

A dicarboxylic acid is a carboxylic acid that contains two carboxyl groups, one at each end of a carbon chain. Saturated acids of this type are named by appending the suffix ***–dioic*** acid to the corresponding alkane name (the –e is retained to facilitate pronunciation). Both carboxyl carbon atoms must be part of the parent carbon chain, and the carboxyl locations need not be specified with numbers because they will always be at the two ends of the chain:



$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

Pentanedioic acid

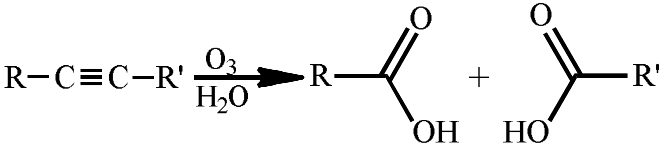


$HO-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH$

2-Methylbutanedioic acid

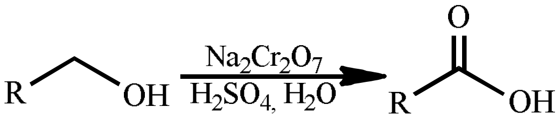
13.2 Preparation of carboxylic acids and acid halides

1. Oxidative cleavage of alkynes. When treated with ozone followed by water, alkynes undergo oxidative cleavage to produce carboxylic acids. Oxidative cleavage will break a triple bond forming two carboxylic acids:



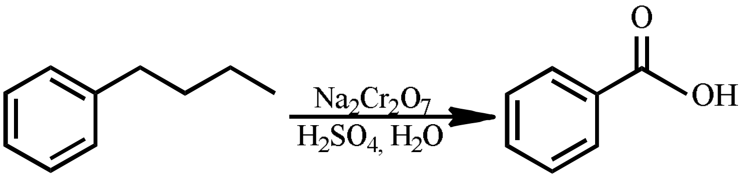
(13.1)

2. Oxidation of primary alcohols. A variety of strong oxidizing agents can be used to oxidize primary alcohols and produce carboxylic acids:



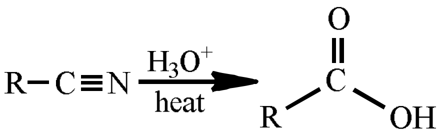
(13.2)

3. Oxidation of alkylbenzenes. Any alkyl group on an aromatic ring will be completely oxidized to give benzoic acid, provided that the benzylic position has at least one hydrogen atom. The oxidation takes place selectively at the benzylic position:



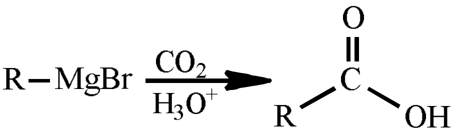
(13.3)

4. Hydrolysis of nitriles. When treated with aqueous acid, a nitrile (a compound with a cyano group) can be converted into a carboxylic acid (reaction 13.4).



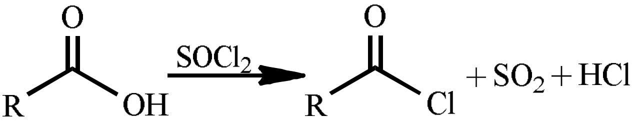
(13.4)

5. Carboxylation of Grignard reagents. Carboxylic acids can also be prepared by treating a Grignard reagent with carbon dioxide:



(13.5)

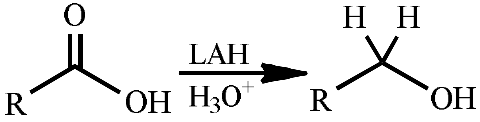
6. Preparation of acid chlorides. Acid chlorides can be formed by treating carboxylic acids with thionyl chloride ($SOCl_2$):



(13.6)

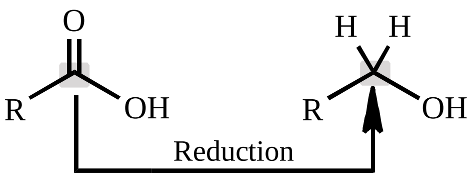
13.3 Reactions of carboxylic acids and acid halides

Carboxylic acids are reduced to alcohols upon treatment with lithium aluminum hydride:

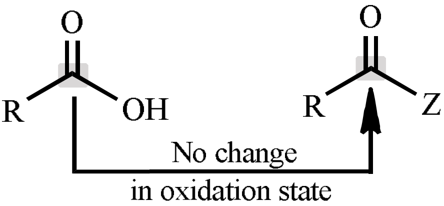


(13.7)

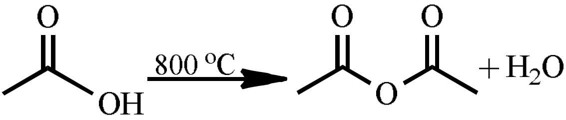
This reaction is a reduction, because the carbon atom of the carboxylic acid moiety is reduced in the process:



Carboxylic acids also undergo many other reactions that do not involve a change in oxidation state:

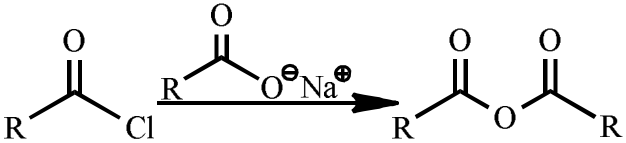


Carboxylic acids can be converted into acid anhydrides with excessive heating:



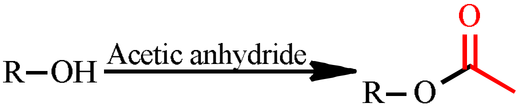
(13.8)

This method is only practical for acetic acid, as most other acids cannot survive the excessive heat. An alternative method for preparing acid anhydrides involves treating an acid chloride with a carboxylate ion, which functions as a nucleophile:



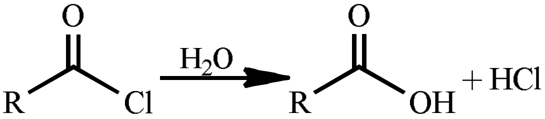
(13.9)

Acetic anhydride is often used to acetylate an alcohol or an amine:



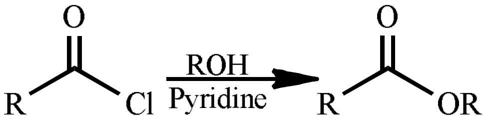
(13.10)

When treated with water, acid chlorides are hydrolyzed to give carboxylic acids:



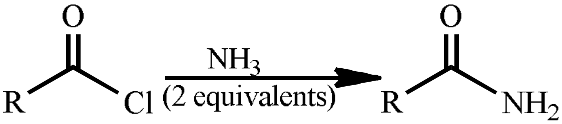
(13.11)

When treated with an alcohol, acid chlorides are converted into esters:



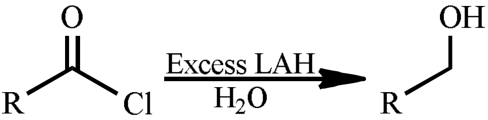
(13.12)

When treated with ammonia, acid chlorides are converted into amides:



(13.13)

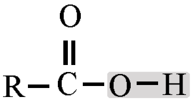
When treated with lithium aluminum hydride, acid chlorides are reduced to give alcohols:



(13.14)

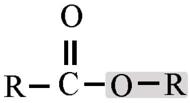
13.4 Esters. Preparation and reactions of esters

An ester is a carboxylic acid derivative in which the –OH portion of the carboxyl group has been replaced with an –OR group:



$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H}$$

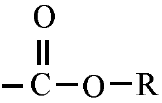
Carboxylic acid



$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R}$$

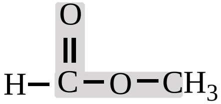
Ester

The ester functional group is thus:



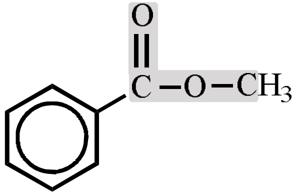
$$\mathrm{-\overset{\overset{\displaystyle O}{\|}}{C}-O-R}$$

The simplest ester, which has two carbon atoms, has a hydrogen atom attached to the ester functional group:

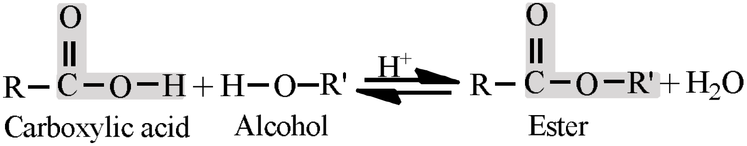


$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_3$$

The structure of the simplest aromatic ester is derived from the structure of benzoic acid, the simplest aromatic carboxylic acid:

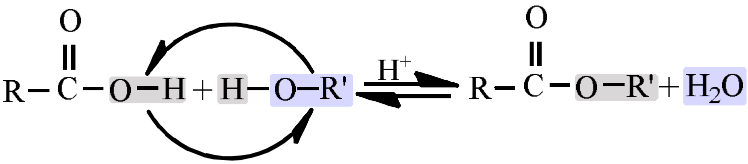


Esters are produced through esterification. An esterification reaction is the reaction of a carboxylic acid with an alcohol (or phenol) to produce an ester. A strong acid catalyst (generally H_2SO_4) is needed for esterification:



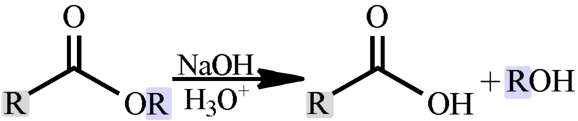
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H+H-O-R' \overset{H^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'+H_2O \qquad (13.15)$$

In the esterification process, a –OH group is lost from the carboxylic acid, a –H atom is lost from the alcohol, and water is formed as a by-product:

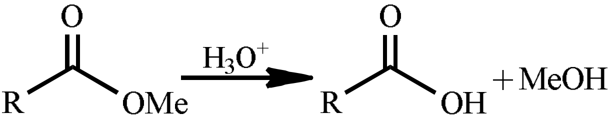


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-H+H-O-R' \overset{H^+}{\rightleftharpoons} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R'+H_2O$$

Esters can be converted into carboxylic acids by treatment with sodium hydroxide followed by an acid. This process is called saponification:

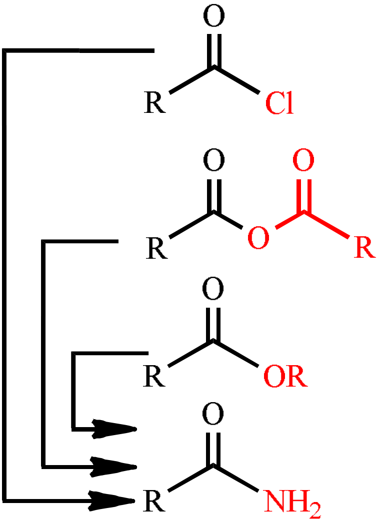

(13.16)

Esters can also be hydrolyzed under acidic conditions:

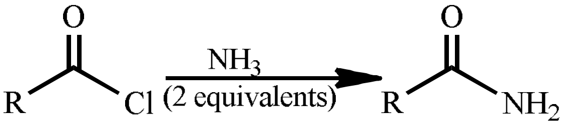

(13.17)

13.5 Amides. Preparation and reactions of amides

Amides can be prepared from any of the carboxylic acid derivatives discussed earlier in this chapter:



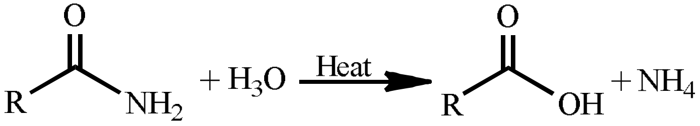
Although they can be prepared in a variety of ways, amides are most efficiently prepared from acid chlorides.



(13.18)

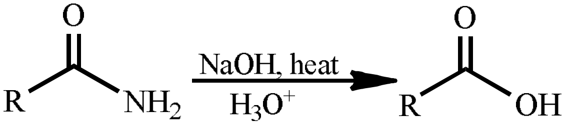
Acid halides are the most reactive of the carboxylic acid derivatives, so the yields are best when an acid chloride is used as a starting material.

Amides can be hydrolyzed to give carboxylic acids in the presence of aqueous acid, but the process is slow and requires heating to occur at an appreciable rate:



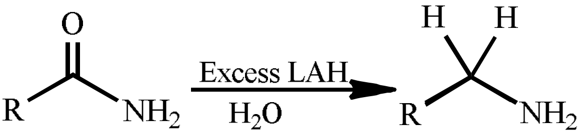
(13.19)

Amides are also hydrolyzed when heated in basic aqueous solutions, although the process is very slow:



(13.20)

When treated with excess LAH, amides are converted into amines:



(13.20)

This is the first reaction we have seen that is somewhat different than the other reactions in this chapter. In this case, the carbonyl group is completely removed.

13.6 Preparation of amines and quaternary ammonium salts

Several methods exist for preparing amines. We consider only one: alkylation in the presence of base. Alkylation under basic conditions is actually a two-step process. In the first step, using a primary amine preparation as an example, an amine salt is produced:

$$NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3X^- \qquad (13.21)$$

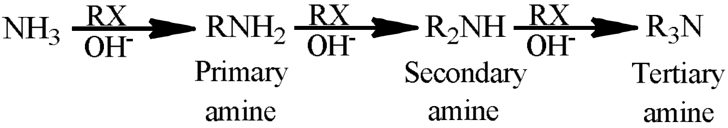
The second step, which involves the base present (NaOH), converts the amine salt to free amine:

$$R-\overset{+}{N}H_3X^- + NaOH \longrightarrow RNH_2 + NaX + H_2O \qquad (13.22)$$

A specific example of the production of a primary amine from ammonia is the reaction of ethyl bromide with ammonia to produce ethylamine. The chemical equation (with both steps combined) is:

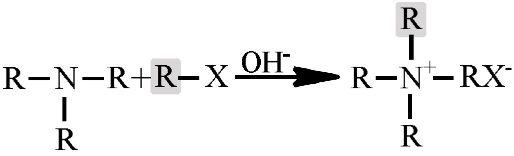
$$NH_3 + CH_3-CH_2-Br + NaOH \longrightarrow CH_3-CH_2-NH_2 + NaBr + H_2O$$

If the newly formed primary amine produced in an ammonia alkylation reaction is not quickly removed from the reaction mixture, the nitrogen atom of the amine may react with further alkyl halide molecules, giving, in succession, secondary and tertiary amines:



$$NH_3 \xrightarrow[OH^-]{RX} \underset{\text{Primary amine}}{RNH_2} \xrightarrow[OH^-]{RX} \underset{\text{Secondary amine}}{R_2NH} \xrightarrow[OH^-]{RX} \underset{\text{Tertiary amine}}{R_3N}$$

Tertiary amines react with alkyl halides in the presence of a strong base to produce a quaternary ammonium salt. A quaternary ammonium salt is an ammonium salt in which all four groups attached to the nitrogen atom of the ammonium ion are hydrocarbon groups:



$$R-\underset{R}{\underset{|}{N}}-R+R-X\xrightarrow{OH^-}R-\overset{R}{\overset{|}{\underset{R}{\underset{|}{N^+}}}}-RX^- \qquad (13.23)$$

Quaternary ammonium salts differ from amine salts in that the addition of a strong base does not convert quaternary ammonium salts back to their “parent” amines; there is no hydrogen atom on the nitrogen with which the OH can react. Quaternary ammonium salts are colorless, odorless, crystalline solids that have high melting points and are usually water-soluble.

CONCEPTS TO REMEMBER

The carboxyl group. The functional group present in carboxylic acids is the carboxyl group. A carboxyl group is composed of a hydroxyl group bonded to a carbonyl carbon atom. It thus contains two oxygen atoms directly bonded to the same carbon atom.

Carboxylic acid derivatives. Four important families of carboxylic acid derivatives are esters, acid chlorides, acid anhydrides, and amides. The group attached to the carbonyl carbon atom distinguishes these derivatives from each other and also from carboxylic acids.

Nomenclature of carboxylic acids. The IUPAC name for a monocarboxylic acid is formed by replacing the final ***-e*** of the hydrocarbon parent name with ***-oic*** acid. As with previous IUPAC nomenclature, the longest carbon chain containing the functional group is identified, and it is numbered starting with the carboxyl carbon atom. Common-name usage is more prevalent for carboxylic acids than for any other type of organic compound.

Types of carboxylic acids. Carboxylic acids are classified by the number of carboxyl groups present (monocarboxylic, dicarboxylic, etc.), by the degree of saturation (saturated, unsaturated, aromatic), and by additional functional groups present (hydroxy, keto, etc.).

Physical properties of carboxylic acids. Low-molecular-mass carboxylic acids are liquids at room temperature and have sharp or unpleasant odors. Long-chain acids are waxlike solids. The carboxyl group is polar and forms hydrogen bonds to other carboxyl groups or other molecules. Thus carboxylic acids have relatively high boiling points, and those with lower molecular masses are soluble in water.

Preparation of carboxylic acids. Carboxylic acids are synthesized through oxidation of primary alcohols or aldehydes using strong oxidizing agents. Aromatic carboxylic acids can be prepared by oxidizing a carbon side chain on a benzene derivative using a strong oxidizing agent.

Acidity of carboxylic acids. Soluble carboxylic acids behave as weak acids, donating protons to water molecules. The portion of the acid molecule left after proton loss is called a carboxylate ion.

Carboxylic acid salts. Carboxylic acids are neutralized by bases to produce carboxylic acid salts. Such salts are usually more soluble in water than are the acids from which they were derived. Carboxylic acid salts are named by changing the ***-ic*** ending of the acid to ***–ate***.

Esters. Esters are formed by the reaction of an acid with an alcohol. In such reactions, the –OR group from the alcohol replaces the –OH group in the carboxylic acid. Esters are polar compounds, but they cannot form hydrogen bonds to each other. Therefore, their boiling points are lower than those of alcohols and acids of similar molecular mass.

Nomenclature of esters. An ester is named as an alkyl (from the name of the alcohol reactant) carboxylate (from the name of the acid reactant).

Chemical reactions of esters. Esters can be converted back to carboxylic acids and alcohols under either acidic or basic conditions. Under acidic conditions, the process is called hydrolysis, and the products are the acid and alcohol. Under basic conditions, the process is called saponification, and the products are the acid salt and alcohol.

Acid chlorides and acid anhydrides. An acid chloride is a carboxylic acid derivative in which the –OH portion of the carboxyl group has been replaced with a –Cl atom. An acid anhydride involves two carboxylic acid molecules bonded together after intermolecular dehydration has occurred. Both acid chlorides and acid anhydrides are very reactive molecules.

Structural characteristics of amides. An amide is derived from a carboxylic acid by replacing the hydroxyl group with an amino or a substituted amino group.

Classification of amides. Amides, like amines, can be classified as primary, secondary, or tertiary, depending on how many nonhydrogen atoms are attached to the nitrogen atom.

Nomenclature for amides. The nomenclature for amides is derived from that for carboxylic acids by changing the ***-oic*** acid ending to ***-amide***. Groups attached to the nitrogen atom of the amide are located using the prefix ***N–***.

Properties of amides. Amides do not exhibit basic properties in solution. Most unbranched amides are solids at room temperature and have correspondingly high boiling points because of strong hydrogen bonds between molecules.

Preparation of amides. Reaction, at elevated temperature, of carboxylic acids with ammonia, primary amines, and secondary amines produces primary, secondary, and tertiary amides, respectively.

Hydrolysis of amides. In amide hydrolysis, the bond between the carbonyl carbon atom and the nitrogen is broken, and free acid and free amine are produced. Acidic hydrolysis conditions convert the product amine to an amine salt. Basic hydrolysis conditions convert the product acid to an acid salt.

Structural characteristics of amines. Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms have been replaced by an alkyl, a cycloalkyl, or an aryl group.

Classification of amines. Amines are classified as primary, secondary or tertiary, depending on the number of hydrocarbon groups (one, two, or three) directly attached to the nitrogen atom. The functional group present in a primary amine, the $–NH_2$ group, is called an amino group. Secondary and tertiary amines contain substituted amino groups.

Nomenclature for amines. Common names for amines are formed by listing the hydrocarbon groups attached to the nitrogen atom in alphabetical order, followed by the suffix -amine. In the IUPAC system, the ***-e*** ending of the name of the longest carbon chain present is changed to -amine, and a number is used to locate the position of the amino group. Carbon-chain substituents are given numbers to designate their locations.

Basicity of amines. Amines are weak bases because of the ability of the unshared electron pair on the amine nitrogen atom to accept a proton in acidic solution.

Amine salts. The reaction of a strong acid with an amine produces an amine salt. Such salts are more soluble in water than are the parent amines.

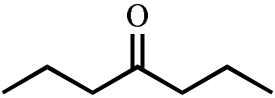
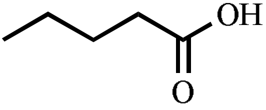
Alkylation of ammonia and amines. Alkylation of ammonia, primary amines, secondary amines, and tertiary amines produces primary amines, secondary amines, tertiary amines, and quaternary ammonium salts, respectively.

INDIVIDUAL TEST PAPER

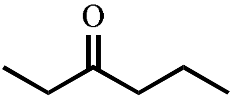
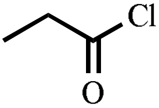
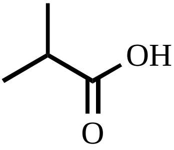
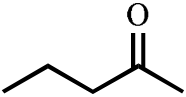
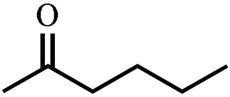
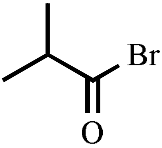
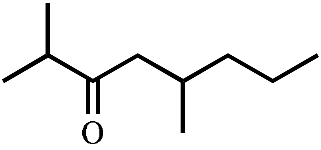
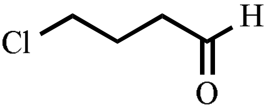
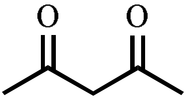
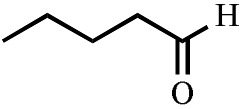
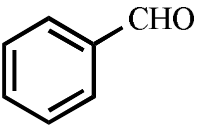
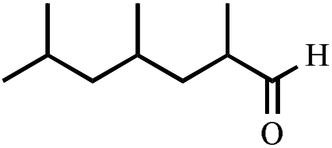
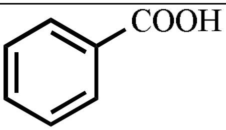
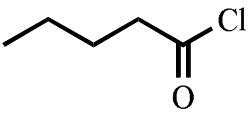
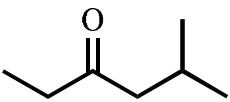
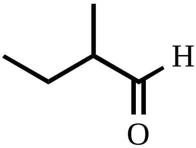
Exercise 1

Name the following alcohols, utilizing IUPAC nomenclature rules (table 13.1).

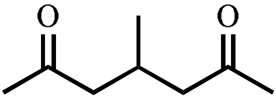
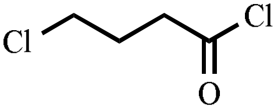
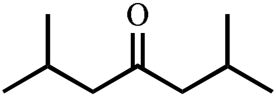
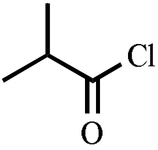
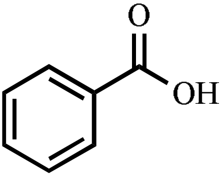
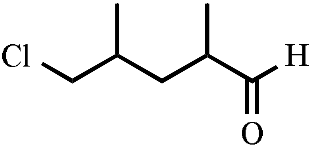
Table 13.1 – Variants of the problem

Variant	Compounds
1	 

Continued of table 13.1

Variant	Compounds	
2		
3		
4		
5		
6		
7		
8		
9		

Continued of table 13.1

Variant	Compounds	
10		
11		
12		

Exercise 2

Draw a structural formula for each of the following carboxylic acids (table 13.2).

Table 13.2 – Variants of the problem

Variant	Compounds	
1	Oxalic acid,	Caproic acid
2	Malonic aci,d	Valeric acid
3	Succinic acid,	Butyric acid
4	Glutaric acid,	Propionic acid
5	Adipic acid,	Acetic acid
6	Pimelic acid,	Formic acid
7	Formic acid,	Pyruvic acid
8	Acetic acid,	Lactic acid
9	Propionic acid,	Glycolic acid

Continued of table 13.2

Variant	Compounds	
10	Butyric acid,	Citric acid
11	Valeric acid,	Fumaric acid
12	Caproic acid,	Malic acid

Exercise 3

Using an acid–base neutralization reaction (with sodium hydroxide), write a chemical equation for the formation of each of the following carboxylic acid salts (table 13.3).

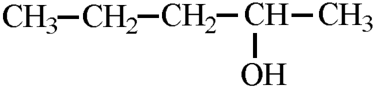
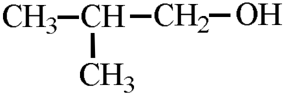
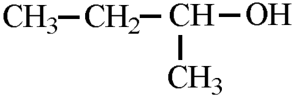
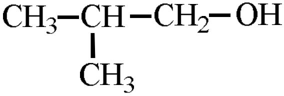
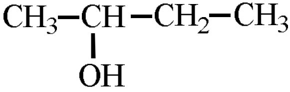
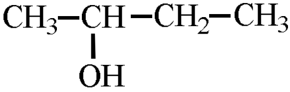
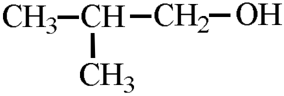
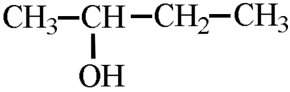
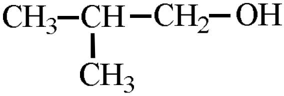
Table 13.3 – Variants of the problem

Variant	Compounds	Variant	Compounds
1	Malic acid, Acetic acid	8	Formic acid, Pimelic acid
2	Caproic acid, Fumaric acid	9	Oxalic acid, Caproic acid
3	Valeric acid, Citric acid	10	Malonic acid, Valeric acid
4	Butyric acid, Glycolic acid	11	Succinic acid, Butyric acid
5	Propionic acid, Lactic acid	12	Glutaric acid, Propionic acid
6	Acetic acid, Pyruvic acid	13	Adipic acid, Acetic acid

Exercise 4

Using an esterification reaction (between the compounds given below), write a chemical equation for the formation of ester. Assign both IUPAC and common names to the ester (table 13.4).

Table 13.4 – Variants of the problem

Variant	Alcohol	
1	 $CH_3-CH_2-CH_2-\underset{OH}{\underset{\mid}{CH}}-CH_3$,	Formic acid
2	 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-OH$,	Acetic acid
3	 $CH_3-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-OH$,	Butyric acid
4	$CH_3-CH_2-CH_2-OH$,	Formic acid
5	$CH_3-CH_2-CH_2-OH$,	Valeric acid
6	 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-OH$,	Propionic acid
7	 $CH_3-\underset{OH}{\underset{\mid}{CH}}-CH_2-CH_3$,	Acetic acid
8	 $CH_3-\underset{OH}{\underset{\mid}{CH}}-CH_2-CH_3$,	Butyric acid
9	$CH_3-CH_2-CH_2-OH$,	Valeric acid
10	 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-OH$,	Formic acid
11	 $CH_3-\underset{OH}{\underset{\mid}{CH}}-CH_2-CH_3$,	Butyric acid
12	 $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-OH$,	Acetic acid

Exercise 5

Write structural equations for each of the following reactions (table 13.5).

Table 13.5 – Variants of the problem

Variant	Compounds
1	Hydrolysis, with an acidic catalyst, of ethyl acetate
2	Saponification, with NaOH, of methyl formate
3	Esterification of propionic acid using propyl alcohol
4	Saponification, with KOH, of methyl acetate
5	Esterification of acetic acid using isopropyl alcohol
6	Hydrolysis, with an acidic catalyst, of ethyl butanate
7	Hydrolysis, with an acidic catalyst, of methyl butanate
8	Saponification, with NaOH, of methyl propanate
9	Esterification of formic acid using butyl alcohol
10	Saponification, with KOH, of ethyl formate
11	Esterification of propionic acid using isopropyl alcohol
12	Hydrolysis, with an acidic catalyst, of ethyl formate

CHAPTER 14

IUPAC nomenclature rules for organic compounds

When relatively few organic compounds were known, chemists arbitrarily named them using what today are called common names. These common names gave no information about the structures of the compounds they described. However, as more organic compounds became known, this nonsystematic approach to naming compounds became unwieldy.

Today, formal systematic rules exist for generating names for organic compounds. These rules, which were formulated and are updated periodically by the International Union of Pure and Applied Chemistry (IUPAC), are known as IUPAC rules. The advantage of the IUPAC naming system is that it assigns each compound a name that not only identifies it but also enables one to draw its structural formula.

14.1 IUPAC nomenclature for alkanes

IUPAC names for the first ten continuous-chain alkanes are given in table 14.1. Note that all of these names end in ***-ane***, the characteristic ending for all ***alkane names***. Note also that beginning with the five-carbon alkane. Greek numerical prefixes are used to denote the actual number of carbon atoms in the continuous chain.

Table 14.1 – IUPAC names for the first ten alkanes

Number of carbonatoms	Name	Molecular formula	Condensed structural formula
1	Methane	CH_4	CH_4
2	Ethane	C_2H_6	CH_3CH_3
3	Propane	C_3H_8	$CH_3CH_2CH_3$
4	Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
5	Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
6	Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
7	Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
8	Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
9	Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
10	Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$

To name branched-chain alkanes, we must be able to name the branch or branches that are attached to the main carbon chain. These branches are formally called substituents. ***A substituent*** is an atom or group of atoms attached to a chain (or ring) of carbon atoms. Note that substituent is a general term that applies to carbon-chain attachments in all organic molecules, not just alkanes.

For branched-chain alkanes, the substituents are specifically called alkyl groups. ***An alkyl group*** is the group of atoms that would be obtained by removing a hydrogen atom from an alkane.

The two most commonly encountered alkyl groups are the two simplest: the one-carbon and two-carbon alkyl groups. Their formulas and names are:

$-CH_3$ Methyl group $-CH_2-CH_3$ Ethyl group

The extra long bond in these formulas (on the left) denotes the point of attachment to the carbon chain. Note that alkyl groups do not lead a stable, independent existence; that is, they are not molecules. They are always found attached to another entity (usually a carbon chain).

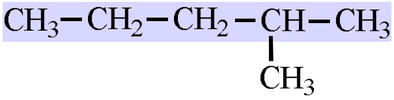
Alkyl groups are named by taking the stem of the name of the alkane that contains the same number of carbon atoms and adding the ending ***-yl***. Table 14.2 gives the names for small continuous-chain alkyl groups.

Table 14.2 – IUPAC names for small alkyl groups

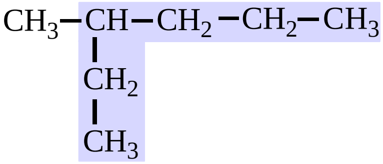
Number of carbons	Structural formula	Stem of alkane name	Alkyl group name
1	$-CH_3$	meth **-yl**	methyl
2	$-CH_2-CH_3$	eth **-yl**	ethyl
3	$-CH_2-CH_2-CH_3$	prop **-yl**	propyl
4	$-CH_2-CH_2-CH_2-CH_3$	but **-yl**	butyl
5	$-CH_2-CH_2-CH_2-CH_2-CH_3$	pent **-yl**	pentyl
6	$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	hex **-yl**	hexyl

14.2 IUPAC rules for naming branched-chain alkanes

Rule 1. Identify the longest continuous carbon chain (the parent chain), which may or may not be shown in a straight line, and name the chain.



$$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

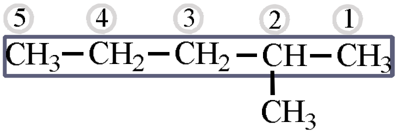


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\underset{\displaystyle CH_2}{\underset{|}{CH}}}}-CH_2-CH_2-CH_3$$

The parent chain name is pentane, because it has five carbon atoms. The parent chain name is hexane, because it has six carbon atoms.

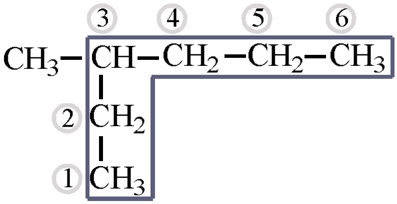
Rule 2. Number the carbon atoms in the parent chain from the end of the chain nearest a substituent (alkyl group).

There always are two ways to number the chain (either from left to right or from right to left). This rule gives the first-encountered alkyl group the lowest possible number.



$$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

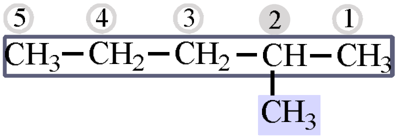
Right-to-left numbering system



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\underset{\displaystyle CH_2}{\underset{|}{CH}}}}-CH_2-CH_2-CH_3$$

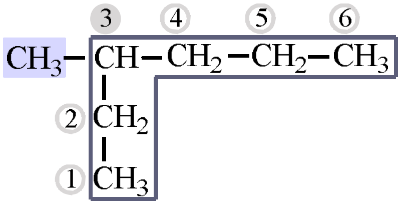
Left-to-right numbering system

Rule 3. If only one alkyl group is present, name and locate it (by number), and prefix the number and name to that of the parent carbon chain.



$$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

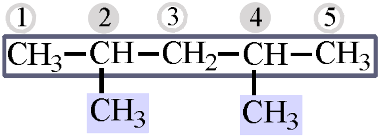
2-Methylpentane



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\underset{\displaystyle CH_2}{\underset{|}{CH}}}}-CH_2-CH_2-CH_3$$

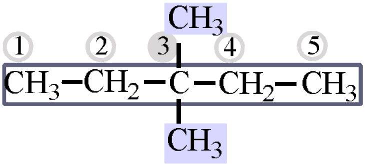
3-Methylhexane

Rule 4. If two or more of the same kind of alkyl group are present in a molecule, indicate the number with a Greek numerical prefix (di-, tri-, tetra-, penta-, and so forth). In addition, a number specifying the location of each identical group must be included. These position numbers, separated by commas, precede the numerical prefix. Numbers are separated from words by hyphens.



$CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_3$

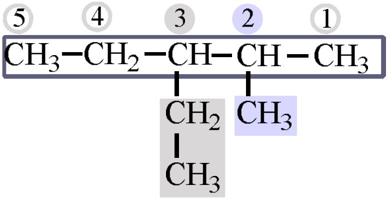
2,4-Dimethylpentane



$CH_3-CH_2-C(CH_3)_2-CH_2-CH_3$

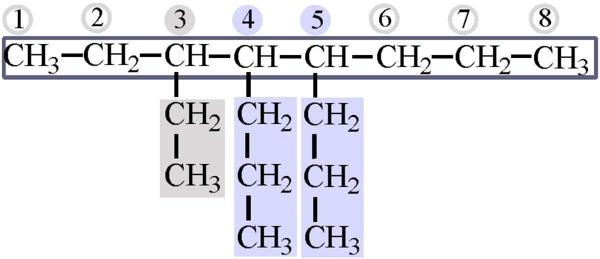
3,3-Dimethylpentane

Rule 5. When two kinds of alkyl groups are present on the same carbon chain, number each group separately, and list the names of the alkyl groups in alphabetical order.



$CH_3-CH_2-CH(CH_2CH_3)-CH(CH_3)-CH_3$

3-Ethyl-2-methylpentane



$CH_3-CH_2-CH(CH_2CH_3)-CH(CH_2CH_2CH_3)-CH(CH_2CH_2CH_3)-CH_2-CH_2-CH_3$

3-Ethyl-4,5-dipropyloctane

Rule 6. Follow IUPAC punctuation rules (Fig. 14.1), which include the following:

1. Separate numbers from each other by commas.
2. Separate numbers from letters by hyphens.
3. Do not add a hyphen or a space between the last-named substituent and the name of the parent alkane that follows.

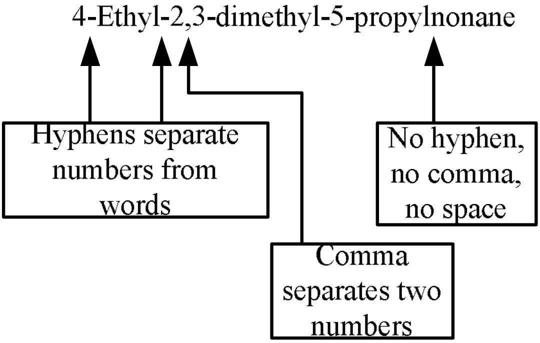


Fig. 14.1 – IUPAC punctuation rules

14.3 IUPAC nomenclature for cycloalkanes

IUPAC naming procedures for cycloalkanes are similar to those for alkanes. The ring portion of a cycloalkane molecule serves as the name base, and the prefix ***cyclo-*** is used to indicate the presence of the ring. Alkyl substituents are named in the same manner as in alkanes. Numbering conventions used in locating substituents on the ring include the following:

1. If there is just one ring substituent, it is not necessary to locate it by number.
2. When two ring substituents are present, the carbon atoms in the ring are numbered beginning with the substituent of higher alphabetical priority and proceeding in the direction (clockwise or

counterclockwise) that gives the other substituent the lower number.

3. When three or more ring substituents are present, ring numbering begins at the substituent that leads to the lowest set of location numbers. When two or more equivalent numbering sets exist, alphabetical priority among substituents determines the set used.

This molecule is a cyclobutane (four-carbon ring) with a methyl substituent (Fig. 14.2). The IUPAC name is simply methylcyclobutane. No number is needed to locate the methyl group, because all four ring positions are equivalent.

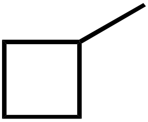


Fig. 14.2 – Methylcyclobutane molecule

This molecule is a cyclopentane with ethyl and methyl substituents (Fig. 14.3). The numbers for the carbon atoms that bear the substituents are 1 and 2. On the basis of alphabetical priority, the number 1 is assigned to the carbon atom that bears the ethyl group. The IUPAC name for the compound is 1-ethyl-2-methylcyclopentane.

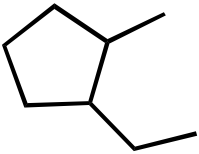


Fig. 14.3 – 1-ethyl-2-methylcyclopentane molecule

This molecule is a dimethylpropyl cyclohexane (Fig. 14.4). Two different 1, 2, 3 numbering systems exist for locating the substituents. On the basis of alphabetical priority, we use the numbering system that has carbon 1 bearing a methyl group; methyl has alphabetical priority over propyl. Thus the compound name is 1,2-dimethyl-3-propylcyclohexane.

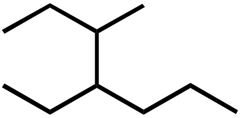


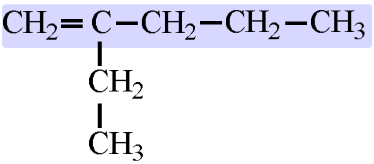
Fig. 14.4 – 1,2-dimethyl-3-propylcyclohexane molecule

14.4 IUPAC nomenclature for alkenes and cycloalkenes

The IUPAC rules previously presented for naming alkanes and cycloalkanes can be used, with some modification, to name alkenes and cycloalkenes.

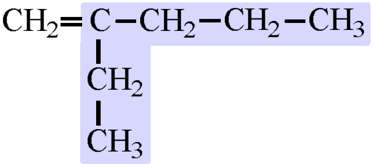
Rule 1. Replace the alkane suffix -ane with the suffix -ene, which is used to indicate the presence of a carbon–carbon double bond.

Rule 2. Select as the parent carbon chain the longest continuous chain of carbon atoms that contains both carbon atoms of the double bond. For example, select:



$$\begin{array}{lllll} CH_2= & C & -CH_2 & -CH_2 & -CH_3 \\ & | & & & \\ & CH_2 & & & \\ & | & & & \\ & CH_3 & & & \end{array}$$

not

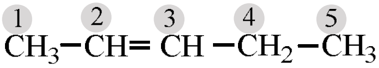


$$\begin{array}{lllll} CH_2= & C & -CH_2 & -CH_2 & -CH_3 \\ & | & & & \\ & CH_2 & & & \\ & | & & & \\ & CH_3 & & & \end{array}$$

Longest carbon chain containing both carbon atoms of the double bond

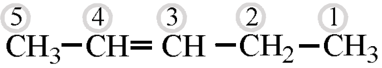
Carbon chain that does not contain both carbon atoms of the double bond

Rule 3. Number the parent carbon chain beginning at the end nearest the double bond.



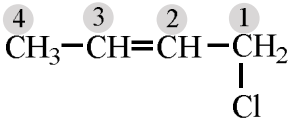
$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-\overset{5}{CH_3}$

not



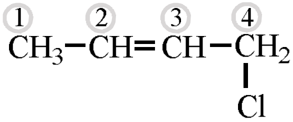
$\overset{5}{CH_3}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH_2}-\overset{1}{CH_3}$

If the double bond is equidistant from both ends of the parent chain, begin numbering from the end closer to a substituent:



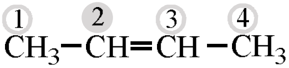
$\overset{4}{CH_3}-\overset{3}{CH}=\overset{2}{CH}-\underset{\underset{Cl}{|}}{\overset{1}{CH_2}}$

not



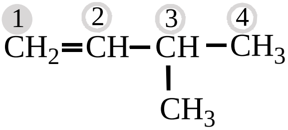
$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{\underset{Cl}{|}}{\overset{4}{CH_2}}$

Rule 4. Give the position of the double bond in the chain as a single number, which is the lower-numbered carbon atom participating in the double bond. This number is placed immediately before the name of the parent carbon chain:



$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_3}$

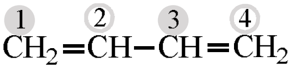
2-Butene



$\overset{1}{CH_2}=\overset{2}{CH}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_3}$

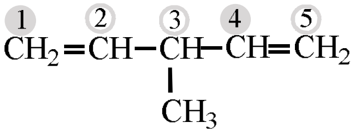
3-Methyl-1-butene

Rule 5. Use the suffixes ***-diene***, ***-triene***, ***-tetrene***, and so on when more than one double bond is present in the molecule. A separate number must be used to locate each double bond:



$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$

1,3-Butadiene

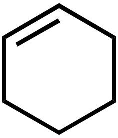


$\overset{1}{CH_2}=\overset{2}{CH}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH}=\overset{5}{CH_2}$

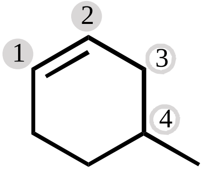
3-Methyl-1,4-pentadiene

Rule 6. Do not use a number to locate the double bond in unsubstituted cycloalkenes with only one double bond because that bond is assumed to be between carbons 1 and 2.

Rule 7. In substituted cycloalkenes with only one double bond, the double-bonded carbon atoms are numbered 1 and 2 in the direction (clockwise or counterclockwise) that gives the first-encountered substituent the lower number. Again, no number is used in the name to locate the double bond.

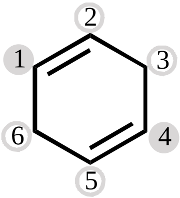


Cyclohexene

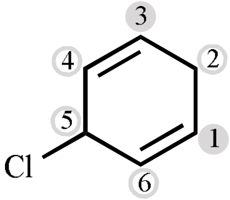


4-Methylcyclohexene

Rule 8. In cycloalkenes with more than one double bond within the ring, assign one double bond the numbers 1 and 2 and the other double bonds the lowest numbers possible:



1,4-Cyclohexadiene



5-Chloro-1,3-cyclohexadiene

14.5 IUPAC nomenclature for alcohols

IUPAC rules for naming alcohols that contain a single hydroxyl group follow.

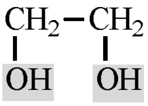
Rule 1. Name the longest carbon chain to which the hydroxyl group is attached. The chain name is obtained by dropping the final ***-e*** from the alkane name and adding the suffix ***-ol.***

Rule 2. Number the chain starting at the end nearest the hydroxyl group, and use the appropriate number to indicate the position of the –OH group. (In numbering of the longest carbon chain, the hydroxyl group has priority over double and triple bonds, as well as over alkyl, cycloalkyl, and halogen substituents.)

Rule 3. Name and locate any other substituents present.

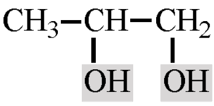
Rule 4. In alcohols where the –OH group is attached to a carbon atom in a ring, the hydroxyl group is assumed to be on carbon 1 (table 14.3).

Polyhydroxy alcohols – alcohols that possess more than one hydroxyl group – can be named with only a slight modification of the preceding IUPAC rules. An alcohol in which two hydroxyl groups are present is named as ***a diol***, one containing three hydroxyl groups is named as ***a triol***, and so on. In these names for diols, triols, and so forth, the final -e of the parent alkane name is retained for pronunciation reasons:



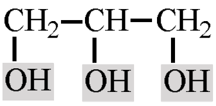
$$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$$

1,2-Ethenediol



$$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$$

1,2-Propanediol



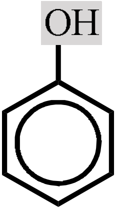
$$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$$

1,2,3-Propanetriol

The first two of the preceding compounds have the common names ethylene glycol and propylene glycol. These two alcohols are synthesized, respectively, from the alkenes ethylene and propylene; hence the common names.

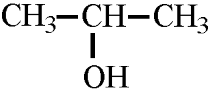
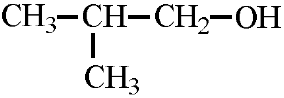
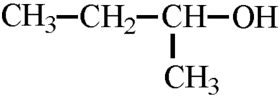
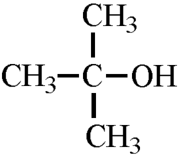
14.6 IUPAC nomenclature for phenols

Besides being the name for a family of compounds, phenol is also the IUPAC-approved name for the simplest member of the phenol family of compounds:

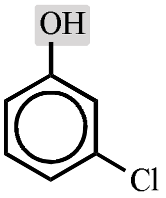


Phenol

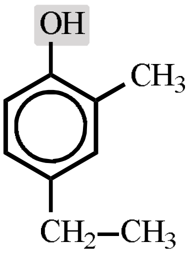
Table 14.3 – Nomenclatures for alcohols

Formula	IUPAC Name
One carbon atom (CH_3OH) CH_3-OH	Methanol
Two carbon atoms (C_2H_5OH) CH_3-CH_2-OH	Ethanol
Three carbon atoms (C_3H_7OH); two constitutional isomers exist	
$CH_3-CH_2-CH_2-OH$	1-propanol
 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_3$	2-propanol
Four carbon atoms (C_4H_9OH); four constitutional isomers exist	
$CH_3-CH_2-CH_2-CH_2-OH$	1-butanol
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-OH$	2-methyl-1-propanol
 $CH_3-CH_2-\underset{CH_3}{\underset{\vert}{CH}}-OH$	2-butanol
 $CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-OH$	2-methyl-2-propanol

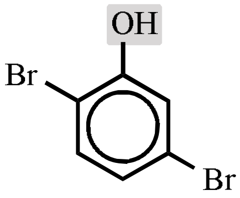
The IUPAC rules for naming phenols are simply extensions of the rules used to name benzene derivatives with hydrocarbon or halogen substituents. The parent name is phenol. Ring numbering always begins with the hydroxyl group and proceeds in the direction that gives the lower number to the next carbon atom bearing a substituent. The numerical position of the hydroxyl group is not specified in the name because it is 1 by definition:



3-Chlorophenol (or *meta*- Chlorophenol)

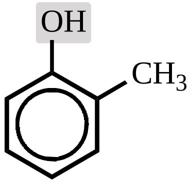


4-Ethyl-2-methylphenol

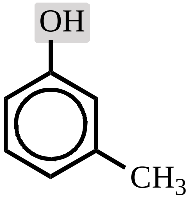


2,5-Dibromophenol

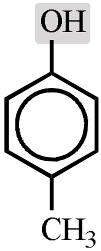
Methyl and hydroxy derivatives of phenol have IUPAC-accepted common names. Methylphenols are called ***cresols***. The name cresol applies to all three isomeric methylphenols.



ortho-Creasol

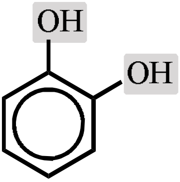


meta-Creasol

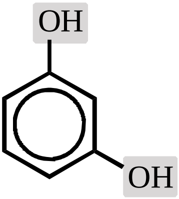


para-Creasol

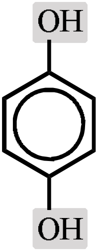
For hydroxyphenols, each of the three isomers has a different common name:



Catechol



Resorcinol



Hydroquinone

14.7 IUPAC nomenclature for ethers

Common names are almost always used for ethers whose alkyl groups contain four or fewer carbon atoms. There are two rules, one for unsymmetrical ethers (two different alkyl/aryl groups) and one for symmetrical ethers (both alkyl/aryl groups the same).

The rules for naming an ether using the IUPAC system are:

Rule 1. Select the longest carbon chain and use its name as the base name.

Rule 2. Change the -yl ending of the other hydrocarbon group to -oxy to obtain the alkoxy group name; methyl becomes methoxy, ethyl becomes ethoxy, etc.

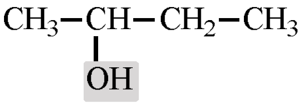
Rule 3. Place the alkoxy name, with a locator number, in front of the base chain name.

$CH_3{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ 1-Methoxybutane

$CH_3{-}CH{-}CH_2{-}O{-}CH_2{-}CH_3$ 1-Ethoxy-2-methylpropane

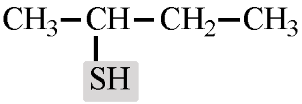
14.8 IUPAC nomenclature for thiols

Thiols are named in the same way as alcohols in the IUPAC system, except that the ***–ol*** becomes ***-thiol***. The prefix ***thio-*** indicates the substitution of a sulfur atom for an oxygen atom in a compound.



$CH_3-\underset{\overset{|}{OH}}{CH}-CH_2-CH_3$

2-Butanol



$CH_3-\underset{\overset{|}{SH}}{CH}-CH_2-CH_3$

2-Butanethiol

14.9 IUPAC nomenclature for aldehydes

The IUPAC rules for naming aldehydes are as follows:

Rule 1. Select as the parent carbon chain the longest chain that includes the carbon atom of the carbonyl group.

Rule 2. Name the parent chain by changing the -e ending of the corresponding alkane name to -al.

Rule 3. Number the parent chain by assigning the number 1 to the carbonyl carbon atom of the aldehyde group.

Rule 4. Determine the identity and location of any substituents, and append this information to the front of the parent chain name.

14.10 IUPAC nomenclature for ketones

Assigning IUPAC names to ketones is similar to naming aldehydes except that the ending ***-one*** is used instead of ***-al***. The rules for IUPAC ketone nomenclature follow.

Rule 1. Select as the parent carbon chain the longest carbon chain that includes the carbon atom of the carbonyl group.

Rule 2. Name the parent chain by changing the -e ending of the corresponding alkane name to -one. This ending, ***-one***, is pronounced "own."

Rule 3. Number the carbon chain such that the carbonyl carbon atom receives the lowest possible number. The position of the carbonyl carbon atom is noted by placing a number immediately before the name of the parent chain.

Rule 4. Determine the identity and location of any substituents, and append this information to the front of the parent chain name.

Rule 5. Cyclic ketones are named by assigning the number 1 to the carbon atom of the carbonyl group. The ring is then numbered to give the lowest number(s) to the atom(s) bearing substituents.

14.11 IUPAC nomenclature for carboxylic acids

A monocarboxylic acid is a carboxylic acid in which one carboxyl group is present. IUPAC rules for naming such compounds are:

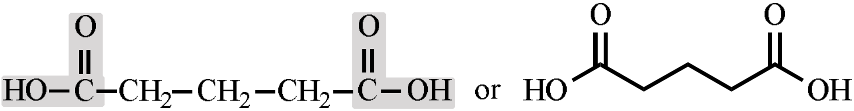
Rule 1. Select as the parent carbon chain the longest carbon chain that includes the carbon atom of the carboxyl group.

Rule 2. Name the parent chain by changing the ***-e*** ending of the corresponding alkane to ***-oic*** acid.

Rule 3. Number the parent chain by assigning the number 1 to the carboxyl carbon atom.

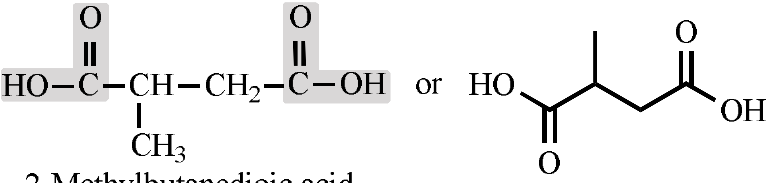
Rule 4. Determine the identity and location of any substituents in the usual manner, and append this information to the front of the parent chain name.

A dicarboxylic acid is a carboxylic acid that contains two carboxyl groups, one at each end of a carbon chain. Saturated acids of this type are named by appending the suffix ***-dioic*** acid to the corresponding alkane name (the ***-e*** is retained to facilitate pronunciation). Both carboxyl carbon atoms must be part of the parent carbon chain, and the carboxyl locations need not be specified with numbers because they will always be at the two ends of the chain:



$$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Pentanedioic acid



$$HO-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

2-Methylbutanedioic acid

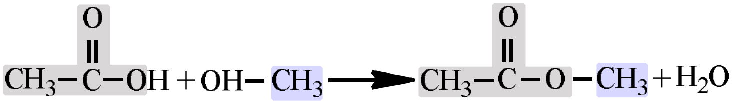
14.2 Nomenclature for esters

Visualizing esters as having an “alcohol part” and an “acid part” is the key to naming them in both the common and the IUPAC systems of nomenclature. The rules are as follows:

Rule 1. :The name for the alcohol part of the ester appears first and is followed by a separate word giving the name for the acid part of the ester.

Rule 2. The name for the alcohol part of the ester is simply the name of the ***R group*** (alkyl, cycloalkyl, or aryl) present in the –OR portion of the ester.

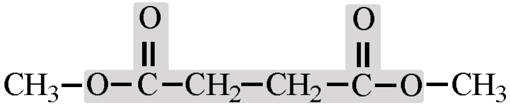
Rule 3. The name for the acid part of the ester is obtained by dropping the ***-ic*** acid ending for the acid’s name and adding the suffix ***-ate***.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + OH-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + H_2O$$

IUPAC:	Ethanoic acid	Methanol	Methyl ethanoate
Common:	Acetic acid	Methyl alcohol	Methyl acetate

Dicarboxylic acids can form diesters, with each of the carboxyl groups undergoing esterification. An example of such a molecule and how it is named is:

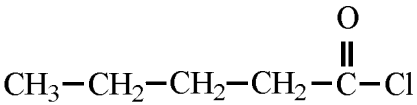


$$CH_3-O-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$$

IUPAC:	Dimethyl butanedioate
Common:	Dimethyl succinate

Acid chlorides are named in either of two ways:

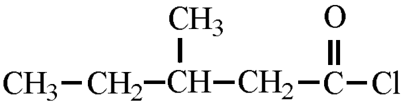
Rule 1. Replace the **-ic** acid ending of the common name of the parent carboxylic acid with **-yl** chloride:



$$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-Cl$$

Butyric acid becomes butyryl chloride.

Rule 2. Replace the ***-oic*** acid ending of the IUPAC name of the parent carboxylic acid with ***-oyl*** chloride:



$$CH_3-CH_2-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-\overset{\overset{\large O}{\|}}{C}-Cl$$

3-Methylpentanoic acid becomes 3-methylpentanoyl chloride.

14.3 Nomenclature for amines

The IUPAC rules for naming amines are similar to those for alcohols. Alcohols are named as alkanols and amines are named as alkanamines. IUPAC rules for naming primary amines are as follows:

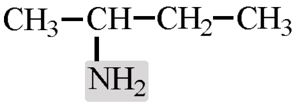
Rule 1. Select as the parent carbon chain the longest chain to which the nitrogen atom is attached.

Rule 2. Name the parent chain by changing the -e ending of the corresponding alkane name to -amine.

Rule 3. Number the parent chain from the end nearest the nitrogen atom.

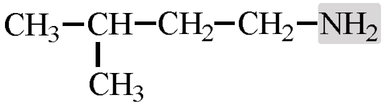
Rule 4. The position of attachment of the nitrogen atom is indicated by a number in front of the parent chain name.

Rule 5. The identity and location of any substituents are appended to the front of the parent chain name:



$$CH_3-\underset{\underset{\large NH_2}{|}}{C}H-CH_2-CH_3$$

2-Butanamine



$$CH_3-\underset{\underset{\large CH_3}{|}}{C}H-CH_2-CH_2-NH_2$$

3-Methyl-1-butanamine

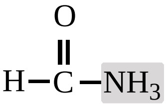
14.4 Nomenclature for amides

For nomenclature purposes (both IUPAC and common), amides are considered to be derivatives of carboxylic acids. Hence their names are based on the name of the parent carboxylic acid.

The rules are as follows:

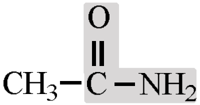
Rule 1. The ending of the name of the carboxylic acid is changed from ***-ic*** acid (common) or ***-oic*** acid (IUPAC) to -amide. For example, benzoic acid becomes benzamide.

Rule 2. The names of groups attached to the nitrogen (2 and 3 amides) are appended to the front of the base name, using an ***N***- prefix as a locator.



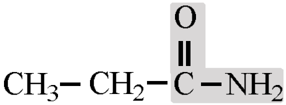
$$H-\overset{\overset{O}{\|}}{C}-NH_3$$

Methanamide
(formamide)



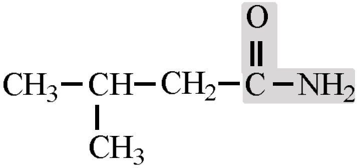
$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$$

Ethanamide
(acetamide)



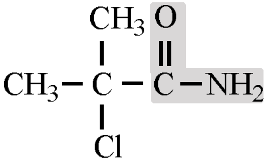
$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2$$

Propanamide
(propionamide)



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-NH_2$$

3-Methylbutanamide
(β-methylbutyramide)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{O}{\|}}{C}-NH_2$$

2-Chloro-2-methylpropanamide
(α-chloro-α-methylpropionamide

APPLICATIONS

Application A

Thermodynamic constants of substances

Molecular formula	Name	$\Delta H^o_{f,298}$, kJ/mol	$S^o{}_{298}$, J/mol·K	$\Delta G^o_{f,298}$, kJ/mol
$Ag_{(s)}$	Silver	0	42,6	0
$Au_{(s)}$	Gold	0	47,4	0
$Be_{(s)}$	Beryllium	0	9,5	0
$Bi_{(s)}$	Bismuth	0	56,9	0
$Cd_{(s)}$	Cadmium	0	51,76	0
$Co_{(s)}$	Cobalt	0	30,04	0
$Cu_{(s)}$	Copper	0	33,15	0
$Fe_{(s)}$	Iron	0	27,2	0
$H_{2(g)}$	Hydrogen	0	130,52	0
$Hg_{(l)}$	Mercury	0	75,9	0
$Mn_{(s)}$	Manganese	0	32,0	0
$Ni_{(s)}$	Nickel	0	29,9	0
$O_{2(g)}$	Oxygen	0	205,0	0
$Pb_{(s)}$	Lead	0	65,8	0
$S_{(s)}$	Sulfur (rhombic)	0,38	32,55	0,19
$S_{(s)}$	Sulfur (monoclinic)	0	31,92	0
$S_{(g)}$	Sulfur	278,81	167,75	238,31
$S_{2(g)}$	Disulfur	128,37	228,03	79,42
$Sb_{(s)}$	Antimony	0	45,69	0
$Si_{(s)}$	Silicon	0	18,8	0
$Sn_{(s)}$	Tin white	0	51,6	0
$Sn_{(s)}$	Tin grey	−2,1	44,1	0,1
$Zn_{(s)}$	Zinc	0	41,6	0
$AgNO_{3(s)}$	Silver (I) nitrate	−124,52	140,92	−33,6
$Ag_2S_{(s)}$	Silver (I) sulfide	−32,6	144,0	−40,7
$AuCl_{3(s)}$	Gold (III) chloride	−118,4	164,4	−53,5

Continued of application A

Molecular formula	Name	$\Delta H^o_{f,298}$, kJ/mol	$S^o{}_{298}$, J/mol·K	$\Delta G^o_{f,298}$, kJ/mol
$BeO_{(s)}$	Beryllium oxide	−598,73	14,14	−569,54
$Be(NO_3)_{2(s)}$	Beryllium (II) nitrate	−700,4	–	–
$Be(NO_3)_{2(l)}$	Beryllium (II) nitrate	−792,2	167,7	−598,9
$Bi(NO_3)_{3(s)}$	Bismuth (III) nitrate	−541,2	–	–
$CdCl_{2(s)}$	Cadmium (II) chloride	−390,79	115,27	−343,24
$Cd(NO_3)_{2(s)}$	Cadmium (II) nitrate	−1236,5	393,0	−1653,2
$Co(OH)_{2(s)}$	Cobalt (II) hydroxide	−541,0	82,0	−456,1
$CuCl_{2(s)}$	Copper (II) chloride	−215,6	108,1	−171,5
$Cu(OH)_{2(s)}$	Copper (II) hydroxide	−444,3	84,0	−359,6
$Fe(NO_3)_{3(l)}$	Iron (III) nitrate	−668,56	132,65	−339,28
$HCl_{(l)}$	Hydrochloric acid	−166,9	56,5	−131,2
$HNO_{3(l)}$	Nitric acid	−173	156,16	−79,9
$H_2O_{(l)}$	Water	−285,83	69,95	−237,23
$H_2S_{(g)}$	Hydrogen sulfide	−20,6	205,7	−33,5
$H_2SO_{4(l)}$	Sulfuric acid	−813,99	156,9	−690,14
$HgCl_{2(s)}$	Mercury (II) chloride	−228,2	140,02	−180,9
$MnCl_{2(s)}$	Manganese (II) chloride	−481,16	118,24	−440,41
$Mn(OH)_{2(s)}$	Manganese (II) hydroxide	−924,66	63,18	−833,75
$NO_{(g)}$	Nitric oxide	91,26	210,64	87,58

Continued of application A

Molecular formula	Name	$\Delta H^{o}_{f,298}$, kJ/mol	S^{o}_{298}, J/mol·K	$\Delta G^{o}_{f,298}$, kJ/mol
$NO_{2(g)}$	Nitrogen dioxide	34,19	240,06	52,29
$NaOH_{(l)}$	Sodium hydroxide	−426,35	64,43	−380,29
$Na_2SiO_{3(s)}$	Sodium silicat	−1561,43	113,76	−1467,5
$Ni(OH)_{2(s)}$	Nickel (II) hydroxide	−454,3	79,9	−458,4
$PH_{3(g)}$	Phoshane	5,44	210,1	13,39
$P_2O_{5(s)}$	Phosphorus pentoxide	−1507,2	140,3	−1371,7
$PbO_{2(s)}$	Lead (IV) oxide	−276,75	71,97	−218,45
$Pb(OH)_{2(s)}$	Lead (II) hydroxide	−512,9	–	−451,55
$Pb(NO_3)_{2(l)}$	Lead (II) nitrate	−451,7	217,9	−258,9
$PbSO_{4(s)}$	Lead (II) sulfate	−912	148,67	−814,3
$SO_{2(g)}$	Sulfur (IV) oxide	−296,9	248,07	−300,21
Sb_2O_5	Antimony (V) oxide	−1008,2	125,2	−865,3
SnO	Tin (II) oxide	−285,98	56,48	−266,88
$Sn(NO_3)_{2(s)}$	Tin (II) nitrate	−456,0	–	–
$Sn(NO_3)_{2(l)}$	Tin (II) nitrate	−425,2	271,7	−250,4
$Zn(OH)_{2(s)}$	Zinc (II) hydroxide	−645,43	76,99	−555,92
$ZnS_{(s)}$	Zinc sulfide	−205,18	57,66	−200,44

Application B

Solubility product (SP) of substances

Substance	SP	Substance	SP
AgBr	$5{,}3\cdot10^{-13}$	Bi_2S_3	$1{,}0\cdot10^{-97}$
AgCN	$1{,}4\cdot10^{-16}$	$CaCO_3$	$4{,}8\cdot10^{-9}$
Ag_2CO_3	$8{,}7\cdot10^{-12}$	CaC_2O_4	$2{,}3\cdot10^{-9}$
$Ag_2C_2O_4$	$1{,}1\cdot10^{-11}$	$CaCrO_4$	$7{,}1\cdot10^{-4}$
AgCl	$1{,}8\cdot10^{-10}$	CaF_2	$4{,}0\cdot10^{-11}$
Ag_2CrO_4	$1{,}1\cdot10^{-12}$	$Ca(OH)_2$	$6{,}3\cdot10^{-6}$
$Ag_2Cr_2O_7$	$1{,}0\cdot10^{-10}$	$Ca_3(PO_4)_2$	$2{,}0\cdot10^{-29}$
AgI	$8{,}3\cdot10^{-17}$	$CaSO_4$	$2{,}5\cdot10^{-5}$
Ag_3PO_4	$1{,}3\cdot10^{-20}$	$Cd(CN)_2$	$1{,}0\cdot10^{-8}$
Ag_2S	$2{,}0\cdot10^{-50}$	$Cd(OH)_2$	$4{,}3\cdot10^{-15}$
Ag_2SO_4	$1{,}2\cdot10^{-5}$	CdS	$1{,}6\cdot10^{-28}$
$Al(OH)_3$	$3{,}7\cdot10^{-15}$	CoC_2O_4	$6{,}3\cdot10^{-8}$
$AlPO_4$	$1{,}7\cdot10^{-19}$	$Co(OH)_2$	$1{,}6\cdot10^{-15}$
$AuCl_3$	$3{,}2\cdot10^{-25}$	CoS	$4{,}0\cdot10^{-21}$
$BaCO_3$	$4{,}0\cdot10^{-10}$	$CsMnO_4$	$9{,}1\cdot10^{-5}$
BaC_2O_4	$1{,}1\cdot10^{-7}$	CuC_2O_4	$2{,}9\cdot10^{-8}$
$BaCrO_4$	$1{,}2\cdot10^{-10}$	CuCN	$3{,}2\cdot10^{-20}$
BaF_2	$1{,}7\cdot10^{-6}$	CuCl	$1{,}2\cdot10^{-6}$
$BaMnO_4$	$2{,}5\cdot10^{-10}$	CuI	$1{,}1\cdot10^{-12}$
$Ba_3(PO_4)_2$	$6{,}0\cdot10^{-39}$	$Cu(OH)_2$	$5{,}6\cdot10^{-20}$
$BaSO_4$	$1{,}1\cdot10^{-10}$	$Cu(OH)_2CO_3$	$1{,}7\cdot10^{-34}$
$Be(OH)_2$	$8{,}0\cdot10^{-22}$	CuS	$6{,}3\cdot10^{-36}$
BiI_3	$8{,}1\cdot10^{-19}$	Cu_2S	$2{,}5\cdot10^{-48}$

Continued of application B

Substance	SP	Substance	SP
FeC_2O_4	$2,1\cdot10^{-7}$	$Mg(OH)_2$	$6,0\cdot10^{-10}$
$Fe(OH)_2$	$8,0\cdot10^{-16}$	$Mn(OH)_2$	$2,3\cdot10^{-13}$
$Fe(OH)_3$	$6,3\cdot10^{-38}$	MnS	$1,1\cdot10^{-13}$
FeS	$5,0\cdot10^{-18}$	$(NH_4)_2IrCl_6$	$3,0\cdot10^{-5}$
Hg_2Br_2	$7,9\cdot10^{-23}$	$Na_3[AlF_6]$	$4,1\cdot10^{-10}$
Hg_2Cl_2	$1,5\cdot10^{-18}$	$Nd(OH)_3$	$7,8\cdot10^{-24}$
Hg_2I_2	$5,4\cdot10^{-29}$	$Ni(CN)_2$	$3,0\cdot10^{-23}$
HgI_2	$1,0\cdot10^{-26}$	$Ni(OH)_2$	$1,6\cdot10^{-14}$
HgS	$1,6\cdot10^{-52}$	NiS	$1,0\cdot10^{-24}$
Hg_2SO_4	$6,2\cdot10^{-7}$	$PbBr_2$	$5,0\cdot10^{-5}$
In_2S_3	$9,1\cdot10^{-84}$	PbC_2O_4	$7,3\cdot10^{-11}$
$K_3[AlF_6]$	$1,6\cdot10^{-9}$	$PbCO_3$	$7,5\cdot10^{-14}$
$KClO_4$	$1,1\cdot10^{-2}$	$PbCl_2$	$1,6\cdot10^{-5}$
$K_3[Co(NO_2)_6]$	$4,3\cdot10^{-10}$	$PbCrO_4$	$1,8\cdot10^{-14}$
$La(OH)_3$	$3,6\cdot10^{-23}$	PbF_2	$2,7\cdot10^{-8}$
$La_2(SO_4)_3$	$3,0\cdot10^{-5}$	PbI_2	$1,1\cdot10^{-9}$
Li_2CO_3	$4,0\cdot10^{-3}$	$Pb_3(PO_4)_2$	$7,9\cdot10^{-43}$
LiF	$1,5\cdot10^{-3}$	PbS	$2,5\cdot10^{-27}$
Li_3PO_4	$3,2\cdot10^{-9}$	$PbSO_4$	$1,6\cdot10^{-8}$
$MgCO_3$	$7,9\cdot10^{-6}$	$PtBr_4$	$3,0\cdot10^{-41}$
MgC_2O_4	$8,6\cdot10^{-5}$	$PtCl_4$	$8,0\cdot10^{-29}$
MgF_2	$6,4\cdot10^{-9}$	Sb_2S_3	$1,6\cdot10^{-93}$
$Mg_3(PO_4)_2$	$3,9\cdot10^{-26}$	$Sc(OH)_3$	$8,7\cdot10^{-28}$
$MgNH_4PO_4$	$2,5\cdot10^{-13}$	$SrCO_3$	$5,3\cdot10^{-10}$

Continued of application B

Substance	SP	Substance	SP
SrC_2O_4	$5{,}6\cdot10^{-8}$	TlCl	$1{,}7\cdot10^{-4}$
$SrCrO_4$	$2{,}7\cdot10^{-5}$	Tl_2CrO_4	$1{,}0\cdot10^{-12}$
SrF_2	$2{,}5\cdot10^{-9}$	Tl_2S	$5{,}0\cdot10^{-21}$
$SrSO_4$	$2{,}1\cdot10^{-7}$	Tl_2SO_4	$4{,}0\cdot10^{-3}$
TlBr	$4{,}3\cdot10^{-6}$	$Zn(CN)_2$	$2{,}6\cdot10^{-13}$
Tl_2CO_3	$4{,}0\cdot10^{-3}$	$Zn(OH)_2$	$1{,}2\cdot10^{-17}$
$Tl_2C_2O_4$	$2{,}0\cdot10^{-4}$	ZnS	$1{,}6\cdot10^{-24}$

Application C

Dissociation constants *Kd* of acids at 298 K

Acid	*Kd*	Acid	*Kd*
H_3AsO_4		H_3PO_4	
K_1	$5{,}6\cdot10^{-3}$	K_1	$7{,}1\cdot10^{-3}$
K_2	$1{,}7\cdot10^{-7}$	K_2	$6{,}2\cdot10^{-8}$
K_3	$3{,}0\cdot10^{-12}$	K_3	$5{,}0\cdot10^{-13}$
H_3AsO_3	$5{,}9\cdot10^{-10}$	H_2O	$1{,}8\cdot10^{-16}$
H_3BO_3	$7{,}1\cdot10^{-10}$	HNO_2	$6{,}9\cdot10^{-4}$
$HBrO_4$	10^{8}	HNO_3	$4{,}4\cdot10$
$HBrO_3$	$2{,}0\cdot10^{-1}$	HI	10^{11}
HBrO	$2{,}2\cdot10^{-9}$	HIO_3	$1{,}7\cdot10^{-1}$
HBr	10^{9}	HIO	$2{,}3\cdot10^{-11}$
H_2SiO_3		H_6TeO_6	
K_1	$2{,}2\cdot10^{-10}$	K_1	$2{,}5\cdot10^{-8}$
K_2	$1{,}6\cdot10^{-12}$	K_2	$1{,}1\cdot10^{-11}$

Continued of application C

Acid	*Kd*	Acid	*Kd*
H_2SO_4		H_2TeO_3	
K_1	$1{,}0\cdot10^{3}$	K_1	$2{,}7\cdot10^{-3}$
K_2	$1{,}2\cdot10^{-2}$	K_2	$1{,}8\cdot10^{-8}$
H_2SO_3			
K_1	$1{,}4\cdot10^{-2}$	$HMnO_4$	10^{8}
K_2	$6{,}2\cdot10^{-8}$		
H_2S		H_2MnO_4	
K_1	$1{,}0\cdot10^{-7}$	K_1	$1{,}0\cdot10^{-1}$
K_2	$2{,}5\cdot10^{-13}$	K_2	$7{,}1\cdot10^{-11}$
H_5IO_6		$H_2S_2O_3$	
K_1	$2{,}5\cdot10^{-2}$	(H_2SO_3S)	
K_2	$4{,}3\cdot10^{-9}$	K_1	$2{,}5\cdot10^{-1}$
K_3	$1{,}0\cdot10^{-15}$	K_2	$1{,}9\cdot10^{-11}$
$H_2O\cdot CO_2$		H_2CrO_4	
K_1	$4{,}5\cdot10^{-7}$	K_1	$1{,}6\cdot10^{-1}$
K_2	$4{,}8\cdot10^{-11}$	K_2	$3{,}2\cdot10^{-7}$
H_3PO_3		H_2Te	
K_1	$3{,}1\cdot10^{-2}$	K_1	$2{,}3\cdot10^{-3}$
K_2	$1{,}6\cdot10^{-7}$	K_2	$6{,}9\cdot10^{-13}$
HPO_2H_2	$5{,}9\cdot10^{-2}$	HCOOH	$1{,}8\cdot10^{-4}$
HF	$6{,}2\cdot10^{-4}$	$HClO_4$	10^{8}
HCl	10^{7}	$HClO_3$	10^{3}
H_2SeO_4			
K_1	$1{,}0\cdot10^{3}$	$HClO_2$	$1{,}1\cdot10^{-2}$
K_2	$1{,}2\cdot10^{-2}$		

Continued of application C

Acid	*Kd*	Acid	*Kd*
H_2Se		H_2SeO_3	
K_1	$1{,}3 \cdot 10^{-4}$	K_1	$1{,}8 \cdot 10^{-3}$
K_2	$1{,}0 \cdot 10^{-11}$	K_2	$3{,}2 \cdot 10^{-9}$
CH_3CO_2H	$1{,}7 \cdot 10^{-5}$	HCN	$5{,}0 \cdot 10^{-10}$
HClO	$3{,}0 \cdot 10^{-8}$	–	–

Application D

Dissociation constants *Kd* of bases at 298 K

Base	*Kd*	Base	*Kd*
$Al(OH)_3$	$1{,}4 \cdot 10^{-9}$	$Ni(OH)_2$	$5{,}0 \cdot 10^{-5}$
$Ca(OH)_2$	$5{,}9 \cdot 10^{-10}$	$Pb(OH)_2$	$3{,}0 \cdot 10^{-8}$
$Cd(OH)_2$	$5{,}0 \cdot 10^{-3}$	$Sc(OH)_3$	$7{,}6 \cdot 10^{-10}$
$Co(OH)_2$	$4{,}0 \cdot 10^{-5}$	$Fe(OH)_2$	$1{,}3 \cdot 10^{-4}$
$Cu(OH)_2$	$3{,}4 \cdot 10^{-7}$	$Fe(OH)_3$	$1{,}8 \cdot 10^{-11}$
$Mg(OH)_2$	$2{,}5 \cdot 10^{-3}$	$Cr(OH)_3$	$1{,}0 \cdot 10^{-10}$
$Mn(OH)_2$	$5{,}0 \cdot 10^{-4}$	$Zn(OH)_2$	$4{,}0 \cdot 10^{-5}$

Навчальне видання

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