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**АНГЛИЙСКИЙ ЯЗЫК  
ПО СПЕЦИАЛЬНОСТИ «ХИМИЯ  
И ТЕХНОЛОГИЯ ОРГАНИЧЕСКИХ  
ВЕЩЕСТВ И МАТЕРИАЛОВ»**

**ENGLISH FOR CHEMISTRY  
AND TECHNOLOGY OF ORGANIC  
SUBSTANCES AND MATERIALS**

**Учебно-методическое пособие  
по английскому языку для студентов II курса  
химико-технологических специальностей**

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**А64 Английский язык по специальности «Химия и технология органических веществ и материалов» : учеб.-метод. пособие по английскому языку для студентов II курса химико-технологических специальностей / сост. : Е. В. Кривоносова, Г. Н. Лесневская, Т. А. Ячная. – Минск : БГТУ, 2016. – 114 с.**

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Учебно-методическое пособие представляет собой комплекс текстов по химико-технологической тематике из оригинальных англоязычных источников и имеет целью развитие и совершенствование у студентов навыков научно-технического перевода, а также усвоение определенного запаса специальных терминов и использование их в устной речи.

Учебно-методическое пособие предназначено как для аудиторных занятий, так и для организации самостоятельной работы студентов.

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# ПРЕДИСЛОВИЕ

Целью настоящего учебно-методического пособия является формирование и совершенствование у студентов навыков работы с профессионально-ориентированной лексикой, навыков научно-технического перевода литературы и употребления специальных терминов в устной речи.

Пособие состоит из 19 разделов, охватывающих практически весь курс органической химии: “Chemical reactions”, “Chemical bonds”, “Isomerism”, “Halogens and their derivatives”, “Ethers and esters”, “Alcohols”, “Carbohydrates”, “Biologically active compounds” и др. Содержание текстового материала соответствует действующей программе по английскому языку для неязыковых вузов. Каждый раздел заканчивается блоком лексических заданий, направленных на закрепление полученных навыков работы с профессионально-ориентированным текстом по специальности.

Для формирования и совершенствования лексических навыков в пособие включены упражнения на соответствие химических терминов и их определений, подстановочные упражнения и др.

Текстовый материал, положенный в основу учебно-методического пособия, взят из оригинальных англоязычных источников, некоторые тексты адаптированы и подвергнуты переработке. Материал подобран с учетом лексических трудностей, которые снимаются по мере прохождения темы, и на основании таких принципов, как информативность, предметная связность, доступность. Соблюдение данных принципов будет способствовать расширению профессионального кругозора, развитию навыков перевода научно-технической литературы, а также усвоению определенного запаса профессиональных терминов. Порядок подачи материала соответствует изучаемым темам по специальности. Повторяемость ключевых слов и выражений, наличие проблемных заданий призваны способствовать выработке у студентов навыков монологической речи.

Использование пособия в учебном процессе позволит ускорить формирование у студентов навыков и умений, необходимых для работы с научно-технической литературой, будет способствовать повышению качества перевода литературы по специальности.

# UNIT I

## ORGANIC CHEMISTRY

In the 17<sup>th</sup> century chemistry was divided into three branches: animal, vegetable, and mineral. It was believed that organic compounds were formed as the result of the so-called “vital force” in living things, and that they could not be produced by the chemists. In 1828, however, Wöhler discovered that ammonium cyanate, a so-called inorganic compound, could be transformed into urea, a typical organic substance.

As the study of organic compounds advanced, it was found that many of them could be prepared in the laboratory from the elements of which they are composed. The sharp distinction between inorganic and organic compounds based on the vital force disappeared. The term organic chemistry has survived, however. Organic chemistry may be defined as the chemistry of the carbon compounds and their reactions because the element carbon is present in all these so-called organic compounds.

Carbon compounds are of two types: inorganic and organic. The compounds that have a mineral origin fall under the category of inorganic compounds. The compounds having plant or animal origin are classified as organic compounds. Lavoisier showed that nearly all compounds of plant origin are composed of carbon, hydrogen and oxygen. While those of animal origin also had other substances like nitrogen, sulphur or phosphorus. Organic chemistry studies the properties of organic carbon compounds.

Carbon (C) is a very special element. It appears in the second row of the periodic table and has four bonding electrons in its valence shell. Similar to other non-metals, carbon needs eight electrons to satisfy its valence shell. Carbon, therefore, forms four bonds with other atoms (each bond consisting of one of carbon's electrons and one of the bonding atom's electrons). Every valence electron participates in bonding, thus carbon atom's bonds will be distributed evenly over the atom's surface. These bonds form a tetrahedron (a pyramid with a spike at the top).

Carbon has the ability to bond with itself to form long chains and ring structures; hence it can form molecules that contain from one to an infinite number of C atoms.

The number of different design possibilities for organic molecules is endless. In order to enable classification of such a large number of molecules, organic chemists have employed the principle of classifying all organic compounds into families according to their functional groups.

## Functional groups

The behavior of any molecule in a particular chemical environment is determined by the stability or reactivity of its bonds. Each different type of bond shows different levels of reactivity. Generally, in a molecule there is a group of more reactive bonds than all the others. This group tends to determine how the whole molecule behaves in a particular chemical environment regardless of the structure of the rest of the molecule. Chemists call these dominant groups of atoms and bonds functional groups. They are used to classify organic compounds into families.

Understanding the types of reactions that functional groups undergo will enable an understanding of how an organic molecule interacts with the environment.

A carbon-carbon double bond is an example of a functional group. Organic compounds that contain a carbon-carbon double bond and no other functional group are called alkenes (a family name used to classify these compounds). All alkenes react with bromine to yield dibromoalkanes.

Hence if you know a functional group reacts in one molecule you can predict how it will react in almost all other molecules.

It is possible to get more than one functional group in a single molecule, but the generalisation stated above still applies.

## Physical properties of an organic substance

In addition to reactivity, the physical properties of an organic substance, such as melting point, boiling point and solubility, are among its most important traits. The physical properties of an organic substance can often be predicted from its structure. In most cases, a substance's molecular weight and the functional groups are sufficient information to estimate the melting point, boiling point, and solubility. Comparing molecules of similar size, the greater the strength of intermolecular force, the more equilibrium will favor the condensed phase at a given pressure and temperature.

## Organic compounds

Millions of carbon compounds have been described in chemical literature, and chemists synthesize many new ones each year.

All organic compounds, such as proteins, carbohydrates, and fats, contain carbon, and all plant and animal cells consist of carbon compounds and their polymers. (Polymers are macromolecules consisting of many simple molecules bonded together in specific ways.) With hydrogen, oxygen, nitrogen, and a few other elements, carbon forms compounds that make up about 18 percent of all the matter in living things. The processes by which organisms consume carbon and return it to their surroundings constitute the carbon cycle.

Study of organic chemistry is important for the simple reason that, organic compounds find applications in almost all aspects of our daily life and properties of organic compounds are distinctly different from those of inorganic compounds.

All living systems obtain their energy from organic compounds like carbohydrates (sugars) and fats, using amino acids and proteins (organic) to grow. They transmit genetic information from one generation to the next through organic compounds called nucleic acids. The clothes we wear are of natural fibres like cotton, while wool or silk or synthetic materials like polyester are organic compounds. Most of the drugs and pharmaceuticals are also organic compounds. In agriculture too, organic chemistry is well represented. Fertilizers like urea, pesticides like DDT, malathion and gammaxene, and plant growth regulators are all organic chemicals. Among various energy sources, fossil fuels like coal, lignite, petroleum and natural gas are of organic origin. Commonly used polymers natural and synthetic like wood, rubber, paper and plastics are again organic compounds.

Organic chemists at all levels are generally employed by pharmaceutical, biotechnical, chemical, consumer product, and petroleum industries.

*Biotechnology* (“biotech” for short) is a field of applied biology that involves using living organisms and bioprocesses to create or modify products for a specific use. The cultivation of plants has been viewed as the earliest example of biotechnology and the precursor to modern genetic engineering and cell and tissue culture technologies. Virtually all biotechnology products are the result of organic chemistry.

Biotechnology is used in health care, crop production and agriculture, nonfood uses of crops and other products (e. g., biodegradable plastics, vegetable oil, biofuels), and environmental applications.

*The chemical industry* is crucial to modern world economies and works to convert raw materials such as oil, natural gas, air, water, metals, and minerals into more than 70,000 different products. These base

products are then used to make consumer products in addition to manufacturing, service, construction, agriculture, and other industries.

Over three-fourths of the chemical industry's output worldwide is polymers and plastics. Chemicals are used to make a wide variety of consumer goods, as well as thousands of products that are inputs to the agriculture, manufacturing, construction, and service industries. The chemical industry itself consumes about a quarter of its own output. Major industrial customers include rubber and plastic products, textiles, petroleum refining, pulp and paper, and primary metals.

*Consumer products* companies make consumer products for everyday use, such as soaps, detergents, cleaning products, plastic goods, and cosmetics.

*The petroleum industry* includes the global processes of exploration, extraction, refining, transporting, and marketing petroleum products. The largest volume products of the industry are fuel oil and gasoline. Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics. The industry is usually divided into three major components: upstream (exploration and production), midstream (transportation), and downstream (refining crude oil, processing and purifying natural gas, creating petrochemicals).

*The pharmaceutical industry* develops, produces, and markets drugs licensed for use as medications for humans or animals.

Organic chemistry is the most important branch of chemistry – but of course, it would be nothing without the many other areas of chemistry – in fact all branches of chemistry should not be viewed in isolation.

## REVISION EXERCISES

### **Ex. 1. Answer the following questions.**

1. What does organic chemistry study? 2. What did Wöhler discover in 1828? 3. Why can carbon form molecules that contain an infinite number of C atoms? 4. What is a functional group? 5. What are the physical properties of an organic substance? 6. What are polymers? 7. Are there many of carbon compounds in the world? 8. What is the carbon cycle? 9. Why are organic compounds worth being studied? 10. Why are organic chemists generally employed by different industries related to chemistry? 11. Is organic chemistry the most important branch of chemistry?

**Ex. 2. Match the words with their definitions.**

- |                 |  |
|-----------------|--|
| 1) DDT          | a) mysterious, metaphysical energies that inhabit “organic” matter and which keep organisms alive and functional   |
| 2) gasoline     | b) to join with each other, to become firmly fixed together  |
| 3) variety      | c) a substance containing atoms from two or more elements  |
| 4) bond         | d) a chemical used to kill insects that harm crops   |
| 5) regardless   | e) one of the substances that combine to form proteins   |
| 6) amino acids  | f) a liquid obtained from petroleum, used mainly for producing power in the engines of cars, trucks                |
| 7) exploration  | g) the act of travelling through a place in order to find out about it or find something such as oil or gold in it |
| 8) vital forces | h) without being affected or influenced by something   |
| 9) pulp         | i) a lot of things of the same type that are different from each other in some way                                 |
| 10) compound    | j) a very soft substance that is almost liquid, made by crushing plants, wood, vegetables etc.                     |

**Ex. 3. Say whether the following statements are true or false.**

1. In the 17<sup>th</sup> century it was believed that the organic compounds cannot be synthesized in the laboratory. 2. Carbon compounds don't have any mineral origin. 3. Wöhler showed that nearly all compounds of plant origin are composed of carbon, hydrogen and oxygen. 4. Carbon can form molecules that contain an infinite number of C atoms. 5. Carbon atom's bonds form a pyramid with a spike at the top. 6. Functional groups are used to determine the molecular weight of the compound. 7. Study of organic chemistry is important because organic compounds are very rare and unique and can hardly be found anywhere. 8. Carbohydrates and fats are sources of energy for all living systems. 9. Biotechnology is used in production of biodegradable plastics, vegetable oil, biofuels. 10. Organic chemists at all levels are generally employed by pharmaceutical, biotechnical, chemical, consumer product, and petroleum industries.

**Ex. 4. Insert the necessary word.**

1. The vast majority of organic compounds are typically chains or rings of ... that contain other elements such as O, N, P, S, Cl, Br and I.  
2. There are over five million of these compounds known today and an

almost ... of new compounds could possibly be synthesized. 3. This can be compared to the total number of ..., which is approximately half a million. 4. Carbon has the ability to bond with itself to form long chains and ... . 5. It can form molecules that ... from one to an infinite number of C atoms. 6. The number of different design possibilities for organic molecules is ... . 7. In order to enable classification of such a large number of molecules, organic chemists have employed the principle of classifying all organic compounds into families according to their ... . 8. This greatly simplifies the study of ... as molecules with the same functional groups behave the same in most chemical reactions.

infinite number, ring structures, carbon atoms, endless, contain, inorganic compounds, functional groups, organic compounds

## UNIT II

# TYPES OF CHEMICAL REACTIONS

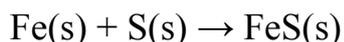
Chemical reaction is a process in which one or more substances, the reactants, are converted to one or more different substances, the products. Substances are either chemical elements or compounds. A chemical reaction rearranges the constituent atoms of the reactants to create different substances as products.

Chemical reactions are an integral part of technology, of culture, and indeed of life itself. Burning fuels, smelting iron, making glass and pottery, brewing beer, and making wine and cheese are among many examples of activities incorporating chemical reactions that have been known and used for thousands of years. Chemical reactions are in large quantities in the geology of Earth, in the atmosphere and oceans, and in a vast array of complicated processes that occur in all living systems.

Chemical reactions must be distinguished from physical changes. Physical changes include changes of state, such as ice melting to water and water evaporating to vapour. If a physical change occurs, the physical properties of a substance will change, but its chemical identity will remain the same. No matter what its physical state, water (H<sub>2</sub>O) is the same compound, in which each molecule is composed of two atoms of hydrogen and one atom of oxygen. However, if water, as ice, liquid, or vapour, encounters sodium metal (Na), the atoms will be redistributed to give the new substances: molecular hydrogen (H<sub>2</sub>) and sodium hydroxide (NaOH). By this, we know that a chemical change or reaction has occurred.

### Basic concepts of chemical reactions

**Synthesis.** When making a new substance from other substances, chemists say that they carry out a synthesis or that they synthesize the new material. Reactants are converted to products, and the process is symbolized by a chemical equation. For example, iron (Fe) and sulfur (S) combine to form iron sulfide (FeS).



The state of matter of reactants and products is designated with the symbols (s) for solids, (l) for liquids, and (g) for gases.

**The conservation of matter.** In reactions under normal conditions matter is neither created nor destroyed, elements are not transformed

into other elements. Therefore, equations depicting reactions must be balanced; that is the same number of atoms of each kind must appear on opposite sides of the equation.

Chemists ordinarily work with weighable quantities of elements and compounds. For example, in the iron-sulfur equation the symbol Fe represents 55.845 grams of iron, S represents 32.066 grams of sulfur, and FeS represents 87.911 grams of iron sulfide. Because matter is not created or destroyed in a chemical reaction, the total mass of reactants is the same as the total mass of products.

The ratio of reactants and products in a chemical reaction is called chemical stoichiometry. Stoichiometry depends on the fact that matter is conserved in chemical processes, and calculations giving mass relationships are based on the concept of the mole. One mole of any element or compound contains the same number of atoms or molecules, respectively, as one mole of any other element or compound. By international agreement, one mole of the most common isotope of carbon (carbon-12) has a mass of exactly 12 grams (this is called the molar mass) and represents  $6.02214179 \times 10^{23}$  atoms (Avogadro's number). One mole of iron contains 55.847 grams; one mole of methane contains 16.043 grams; one mole of molecular oxygen is equivalent to 31.999 grams; and one mole of water is 18.015 grams. Each of these masses represents  $6.0221 \times 10^{23}$  molecules.

**Energy considerations.** Energy plays a key role in chemical processes. According to the modern view of chemical reactions, bonds between atoms in the reactants must be broken, and the atoms or pieces of molecules are reassembled into products by forming new bonds. Energy is absorbed to break bonds, and energy is evolved as bonds are made. In some reactions the energy required to break bonds is larger than the energy evolved on making new bonds, and the net result is the absorption of energy. Such a reaction is said to be endothermic if the energy is in the form of heat. The opposite of endothermic is exothermic; in an exothermic reaction, energy as heat is evolved. The more general terms *exoergic* (energy evolved) and *endoergic* (energy required) are used when forms of energy other than heat are involved.

Entropy is important in determining the favourability of a reaction. Entropy is a measure of the number of ways in which energy can be distributed in any system. Entropy accounts for the fact that not all energy available in a process can be manipulated to do work. The entropy

of the reacting system increases during combustion. Just as important, the heat energy transferred by the combustion to its surroundings increases the entropy in the surroundings. The total of entropy changes for the substances in the reaction and the surroundings is positive, and the reaction is product-favoured.

***Kinetic considerations.*** Chemical reactions commonly need an initial input of energy to begin the process. Although the combustion of wood, paper, or methane is an exothermic process, a burning match or a spark is needed to initiate this reaction. The energy supplied by a match arises from an exothermic chemical reaction that is itself initiated by the frictional heat generated by rubbing the match on a suitable surface.

In some reactions, the energy to initiate a reaction can be provided by light. Numerous reactions in earth's atmosphere are photochemical, or light-driven, reactions initiated by solar radiation. One example is transformation of ozone ( $O_3$ ) into oxygen ( $O_2$ ) in the troposphere.

The reaction must also occur at an observable rate. Several factors influence reaction rates, including the concentrations of reactants, the temperature, and the presence of catalysts. The concentration affects the rate at which reacting molecules collide, a prerequisite for any reaction. Temperature is influential because reactions occur only if collisions between reactant molecules are sufficiently energetic. The proportion of molecules with sufficient energy to react is related to the temperature. Catalysts affect rates by providing a lower energy pathway by which a reaction can occur. Among common catalysts are precious metal compounds used in automotive exhaust systems that accelerate the breakdown of pollutants such as nitrogen dioxide into harmless nitrogen and oxygen. A wide variety of biochemical catalysts are also known, including chlorophyll in plants (which facilitates the reaction by which atmospheric carbon dioxide is converted to complex organic molecules such as glucose) and many biochemical catalysts called enzymes. The enzyme pepsin, for example, assists in the breakup of large protein molecules during digestion.

### **Classification of chemical reactions**

Chemists classify reactions in a number of ways: a) by the type of product; b) by the types of reactants; c) by reaction outcome; d) by reaction mechanism. Often, a given reaction can be placed in two or even three categories.

## Classification by type of product

**Gas-forming reactions.** Many reactions produce a gas such as carbon dioxide, hydrogen sulfide ( $\text{H}_2\text{S}$ ), ammonia ( $\text{NH}_3$ ), or sulfur dioxide ( $\text{SO}_2$ ). An example of a gas-forming reaction is that which occurs when a metal carbonate such as calcium carbonate ( $\text{CaCO}_3$ , the chief component of limestone, seashells, and marble) is mixed with hydrochloric acid ( $\text{HCl}$ ) to produce carbon dioxide:



In this equation, the symbol (aq) signifies that a compound is in an aqueous, or water, solution.

**Precipitation reactions.** Formation of an insoluble compound will sometimes occur when a solution containing a particular cation (a positively charged ion) is mixed with another solution containing a particular anion (a negatively charged ion). The solid that separates is called a precipitate.

Compounds having anions such as sulfide ( $\text{S}^{2-}$ ), hydroxide ( $\text{OH}^-$ ), carbonate ( $\text{CO}_3^{2-}$ ), and phosphate ( $\text{PO}_4^{3-}$ ) are often insoluble in water. A precipitate will form if a solution containing one of these anions is added to a solution containing a metal cation such as  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , or  $\text{Al}^{3+}$ . Minerals are water-insoluble compounds. Precipitation reactions in nature can account for mineral formation in many cases, such as with undersea vents called “black smokers” that form metal sulfides.

## Classification by types of reactants

**Oxidation-reduction reactions.** Oxidation-reduction (redox) reactions involve the transfer of one or more electrons from a reducing agent to an oxidizing agent. This has the effect of reducing the real or apparent electric charge on an atom in the substance being reduced and of increasing the real or apparent electric charge on an atom in the substance being oxidized. Carbon atoms may have any oxidation state from  $-4$  (e. g.  $\text{CH}_4$ ) to  $+4$  (e. g.  $\text{CO}_2$ ), depending upon their substituents. Fortunately, we need not determine the absolute oxidation state of each carbon atom in a molecule, but only the change in oxidation state of those carbons involved in a chemical transformation. To determine whether a carbon atom has undergone a redox change during a reaction we simply note any changes in the number of bonds to hydrogen and the number of bonds to more electronegative atoms that has occurred. Bonds to other carbon atoms are ignored.

Simple redox reactions include the reactions of an element with oxygen. For example, magnesium burns in oxygen to form magnesium oxide (MgO). Redox reactions are the source of the energy of batteries. The electric current generated by a battery arises because electrons are transferred from a reducing agent to an oxidizing agent through the external circuitry.

**Acid-base reactions.** Acids and bases are important compounds in the natural world, so their chemistry is central to any discussion of chemical reactions. First, acid-base reactions are among the simplest to recognize and understand. Second, some classes of organic compounds have distinctly acidic properties, and some other classes behave as bases, so we need to identify these aspects of their chemistry. Finally, many organic reactions are catalyzed by acids and/or bases. Organic chemists use two acid-base theories for interpreting and planning their work: the bronsted – lowry theory and the lewis theory.

### Classification by reaction result

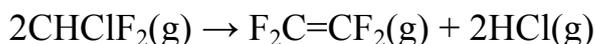
**Decomposition reactions.** Decomposition reactions are processes in which chemical species break up into simpler parts. Usually, decomposition reactions require energy input. For example, a common method of producing oxygen gas in the laboratory is the decomposition of potassium chlorate (KClO<sub>3</sub>) by heat.

Another decomposition reaction is the production of sodium (Na) and chlorine (Cl<sub>2</sub>) by electrolysis of molten sodium chloride (NaCl) at high temperature.

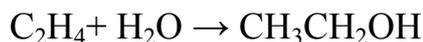
A decomposition reaction that was very important in the history of chemistry is the decomposition of mercury oxide (HgO) with heat to give mercury metal (Hg) and oxygen gas. This is the reaction used by 18<sup>th</sup> century chemists Carl Wilhelm Scheele, Joseph Priestley, and Antoine-Laurent Lavoisier in their experiments on oxygen.

**Substitution, elimination and addition reactions.** These terms are particularly useful in describing organic reactions. In a substitution reaction, an atom or group of atoms in a molecule is replaced by another atom or group of atoms. For example, methane (CH<sub>4</sub>) reacts with chlorine (Cl<sub>2</sub>) to produce chloromethane (CH<sub>3</sub>Cl), a compound used as a topical anesthetic. In this reaction, a chlorine atom is substituted for a hydrogen atom. Substitution reactions are widely used in industrial chemistry. For example, substituting two of the chlorine atoms on chloroform (CHCl<sub>3</sub>) with fluorine atoms produces chlorodi-

fluoromethane ( $\text{CHClF}_2$ ). This product undergoes a further reaction when heated strongly:



This latter reaction is an example of an elimination reaction, a hydrogen atom and a chlorine atom being eliminated from the starting material as hydrochloric acid (HCl). The other product is tetrafluoroethylene, a precursor to the polymer known commercially as Teflon. Addition reactions are the opposite of elimination reactions. As the name implies, one molecule is added to another. An example is the common industrial preparation of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). Historically, this compound was made by fermentation. However, since the early 1970, it has also been made commercially by the addition of water to ethylene:



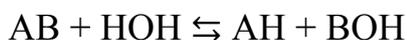
**Polymerization reactions.** Polymers are high-molecular-weight compounds, formed by the aggregation of many smaller molecules called monomers. The plastics that have so changed society and the natural and synthetic fibres used in clothing are polymers. There are two basic ways to form polymers: a) linking small molecules together, a type of addition reaction; b) combining two molecules (of the same or different type) with the elimination of a stable small molecule such as water. This latter type of polymerization combines addition and elimination reactions and is called a condensation reaction.

An example of the first type of reaction is the union of thousands of ethylene molecules that gives polyethylene. Other addition polymers include polypropylene (made by polymerizing  $\text{H}_2\text{C}=\text{CHCH}_3$ ), polystyrene (from  $\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$ ), and polyvinyl chloride (from  $\text{H}_2\text{C}=\text{CHCl}$ ).

Starch and cellulose are examples of the second type of polymer. These are members of a class of compounds called carbohydrates, substances with formulas that are multiples of the simple formula  $\text{CH}_2\text{O}$ . Both starch and cellulose are polymers of glucose, a sugar with the formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . In both starch and cellulose, molecules of glucose are joined together with concomitant elimination of a molecule of water for every linkage formed.

**Solvolysis and hydrolysis.** A solvolysis reaction is one in which the solvent is also a reactant. Solvolysis reactions are generally named after the specific solvent. The term hydrolysis is used when

water is involved. If a compound is represented by the formula AB (in which A and B are atoms or groups of atoms) and water is represented by the formula HOH, the hydrolysis reaction may be represented by the reversible chemical reaction:



Hydrolysis of an organic compound is illustrated by the reaction of water with esters. The hydrolysis of an ester produces an acid and an alcohol.

Hydrolysis reactions play an important role in chemical processes that occur in living organisms. Proteins are hydrolyzed to amino acids, fats to fatty acids and glycerol, and starches and complex sugars to simple sugars. In most instances, the rates of these processes are enhanced by the presence of enzymes, biological catalysts. Hydrolysis reactions are also important to acid-base behaviour. Hydrolysis reactions account for the basic character of many common substances.

### **Classification by reaction mechanism**

In modern organic chemistry organic reactions can be classified by their mechanisms. A detailed description of the changes in structure and bonding that take place in the course of a reaction, and the sequence of such events is called the reaction mechanism. A reaction mechanism should include a representation of possible electron reorganization, as well as the identification of any intermediate species that may be formed as the reaction progresses. In studying the reaction mechanisms, we ascertain the order and the way old chemical bonds are broken and new ones are made in the course of a reaction. When we classify reactions by their mechanisms, our attention is attracted above all by the way a covalent bond in a reacting molecule is cleaved. Since chemical reactions involve the breaking and making of bonds, a consideration of the movement of bonding (and non-bonding) valence shell electrons is essential to this understanding. If a covalent single bond is broken so that one electron of the shared pair remains with each fragment, this bond-breaking is called homolysis. If the bond breaks with both electrons of the shared pair remaining with one fragment, this is called heterolysis. The products of bond breaking are not stable in the usual sense, and cannot be isolated for prolonged study. Such species are referred to as reactive intermediates.

Reaction mechanisms provide details on how atoms are shuffled and reassembled in the formation of products from reactants.

**Chain reactions.** Chain reactions occur in a sequence of steps, in which the product of each step is a reagent for the next. Chain reactions generally involve three distinct processes: an initiation step that begins the reaction, a series of chain-propagation steps, and, eventually, a termination step.

Polymerization reactions are chain reactions, and the formation of Teflon from tetrafluoroethylene is one example. In this reaction, a peroxide (a compound in which two oxygen atoms are joined together by a single covalent bond) may be used as the initiator. Peroxides readily form highly reactive free-radical species (a species with an unpaired electron) that initiate the reaction.

**Photolysis reactions.** Photolysis reactions are initiated or sustained by the absorption of electromagnetic radiation. One example is the decomposition of ozone to oxygen in the atmosphere. Another example is the synthesis of chloromethane from methane and chlorine, which is initiated by light. This reaction, coincidentally, is also a chain reaction. It begins with the endothermic reaction of a chlorine molecule ( $\text{Cl}_2$ ) to give chlorine atoms, a process that occurs under ultraviolet irradiation. When formed, some of the chlorine atoms recombine to form chlorine molecules, but not all do so. If a chlorine atom instead collides with a methane molecule, a two-step chain propagation occurs. The first propagation step produces the methyl radical ( $\text{CH}_3$ ). This free-radical species reacts with a chlorine molecule to give the product and a chlorine atom, which continues the chain reaction for many additional steps. Possible termination steps include combination of two methyl radicals to form ethane ( $\text{CH}_3\text{CH}_3$ ) and a combination of methyl and chlorine radicals to give chloromethane.

## REVISION EXERCISES

### Ex. 1. Answer the following questions.

1. How do we call a process when one or more substances are converted into one or more different substances? 2. When did the concept of a chemical reaction appear? 3. What is synthesis? 4. How is the ratio of reactants and products in a chemical reaction called? 5. What reaction is said to be endothermic? 6. What conditions are necessary to begin a reaction? 7. What factors influence the reaction rate?

**Ex. 2. Match the words with their definitions.**

- |                 |   |
|-----------------|---|
| 1) precipitate  | a) a large molecule consisting of chains or rings of linked monomer units, usually characterized by high melting and boiling points                 |
| 2) reduction    | b) a chemical reaction in which the solute and solvent react to form a new compound   |
| 3) elimination  | c) an insoluble solid that emerges from a liquid solution   |
| 4) fermentation | d) any chemical reaction that involves the gaining of electrons   |
| 5) polymer      | e) a polysaccharide that is composed of glucose monomers and is the main constituent of the cell wall of plants                                     |
| 6) cellulose    | f) any of a group of chemical reactions induced by microorganisms or enzymes that split complex organic compounds into relatively simple substances |
| 7) solvolysis   | g) a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism                           |

**Ex. 3. Say whether the following statements are true or false.**

1. A chemical reaction rearranges the constituent atoms of the reactants to create different substances. 2. In reactions under normal conditions matter is neither created nor destroyed. 3. One mole of any element or compound contains different number of atoms or molecules. 4. Entropy is a measure of the number of ways in which energy can be distributed in any system. 5. Starch and cellulose are members of a class of compounds called hydrocarbons. 6. If the bond breaks with both electrons of the shared pair remaining with one fragment, this is called homolysis. 7. A detailed description of the changes in structure and bonding that take place in the course of a reaction, and the sequence of such events is called the reaction mechanism.

**Ex. 4. Insert the necessary word.**

1. When making a new substance from other substances, chemists say that they carry out a ... . 2. In an ... reaction, energy as heat is evolved. 3. Chemical reactions commonly need an initial input of ... to begin the process. 4. Several factors influence ... rates, including the concentrations of reactants, the temperature, and the presence of catalysts. 5. The ... that separates is called a precipitate. 6. Simple ... reactions include the reactions of an element with oxygen. 7. ... reactions occur in a sequence of steps in which the product of each step is a reagent for the next.

energy, synthetic, chain, reaction, redox, exothermic, solid
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## **UNIT III**

# **TYPES OF BONDS**

Chemical bonds allow all of the elements to combine in a variety of ways to create everything on Earth. Without these chemical bonds life as we know it would not be able to exist as every living organism is created from compounds of elements that work together in specific ways.

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The strength of chemical bonds varies considerably; there are “strong bonds” such as covalent or ionic bonds and “weak bonds” such as Dipole-dipole interaction, the London dispersion force and hydrogen bonding.

Since opposite charges attract via a simple electromagnetic force, the negatively charged electrons that are orbiting the nucleus and the positively charged protons in the nucleus attract each other. An electron positioned between two nuclei will be attracted to both of them, and the nuclei will be attracted toward electrons in this position. This attraction constitutes the chemical bond. A chemical bond is a region that forms when electrons from different atoms interact with each other. The electrons that participate in chemical bonds are the valence electrons, which are the electrons found in an atom’s outermost shell.

In general, strong chemical bonding is associated with the sharing or transfer of electrons between the participating atoms. The atoms in molecules, crystals, metals and diatomic gases are held together by chemical bonds, which dictate the structure and the bulk properties of matter. The number of bonds an atom forms corresponds to its valence. The amount of energy required to break a bond and produce neutral atoms is called the bond energy. All bonds arise from the attraction of unlike charges according to Coulomb’s law. The principal types of a chemical bond are the ionic, covalent, metallic, and hydrogen bonds. The ionic and covalent bonds are idealized cases, however; most bonds are of an intermediate type.

### **Ionic bonds**

An ionic bond is formed when one atom accepts or donates one or more of its valence electrons to another atom. These chemical bonds are created between ions where one is a metal and one is a non-metal element. When an atom (or group of atoms) gains or loses one or more electrons, it forms an ion. Ions have either a net positive or net negative

charge. Positively charged ions are attracted to the negatively charged 'cathode' in an electric field and are called cations. Anions are negatively charged ions named as a result of their attraction to the positive 'anode' in an electric field. Every ionic chemical bond is made up of at least one cation and one anion.

The atoms of metallic elements, e. g., those of sodium, lose their outer electrons easily, while the atoms of nonmetals, e. g., those of chlorine, tend to gain electrons. The highly stable ions that result retain their individual structures as they approach one another to form a stable molecule or crystal. Sodium chloride (NaCl) is the classic example of ionic bonding

Ionic bonding is not limited by simple binary systems, however. An ionic bond can occur at the center of a large covalently bonded organic molecule such as an enzyme. In this case, a metal atom, like iron, is both covalently bonded to large carbon groups and ionically bonded to other simpler inorganic compounds (like oxygen).

Ionic bonds form many compounds every day.

### Covalent bonds

A single covalent bond is created when two atoms share a pair of electrons. If the atoms share more than two electrons, double and triple bonds are formed, because each shared pair produces its own bond.

By sharing their electrons, both atoms are able to achieve a highly stable electron configuration corresponding to that of an inert gas. Multiple covalent bonds are common for certain atoms depending upon their valence configuration. For example, a double covalent bond, which occurs in ethylene (C<sub>2</sub>H<sub>4</sub>), results from the sharing of two sets of valence electrons. Atomic nitrogen (N<sub>2</sub>) is an example of a triple covalent bond.

The polarity of a covalent bond is defined by any difference in electronegativity of the two participating atoms. Bond polarity describes the distribution of electron density around two bonded atoms. For two bonded atoms with similar electronegativities, the electron density of the bond is equally distributed between the two atoms. This is a *nonpolar* covalent bond. The electron density of a covalent bond is shifted towards the atom with the largest electronegativity. This is a *polar* covalent bond.

A *coordinate* covalent bond is formed when one atom donates both of the electrons to form a single covalent bond. These electrons

originate from the donor atom as an unshared pair. Some elements form very large molecules by forming covalent bonds. When these molecules repeat the same structure over and over in the entire piece of material, the bonding of the substance is called *network* covalent.

Covalent bonds are of particular importance in organic chemistry because of the ability of the carbon atom to form four covalent bonds. These bonds are oriented in definite directions in space, giving rise to the complex geometry of organic molecules.

### **Metallic and hydrogen bonds**

Unlike the ionic and covalent bonds, which are found in a great variety of molecules, the metallic and hydrogen bonds are highly specialized.

The metallic bond is responsible for the crystalline structure of pure metals. This bond cannot be ionic because all the atoms are identical, nor can it be covalent, in the ordinary sense, because there are too few valence electrons to be shared in pairs among neighboring atoms. Instead, the valence electrons are shared collectively by all the atoms in the crystal. This is the strongest of the three major bonds because the electrons are shared in more than just the first shells. The more shells involved in sharing electrons, the stronger the bond. Compounds formed by metallic bonds do not completely break until the metal is boiled, usually at a very high temperature. Steel is an example of a metallic bond. Without metallic bonds and the properties of metal modern life would not be possible. Steel is used extensively in every modern society. Metal is also used in electronics that form the basic components in computers and other essential modern conveniences.

Hydrogen bonding occurs between a hydrogen atom and an electronegative atom, e. g., oxygen, fluorine, chlorine. It's a strong electrostatic attraction between two independent polar molecules, i. e., molecules in which the charges are unevenly distributed. The bond is much weaker than an ionic or a covalent bond, but stronger than van der Waals forces. A hydrogen bond is classified as a type of weak chemical bond. It is responsible for the structure of ice.

The reason hydrogen bonding occurs is because the electron is not shared evenly between a hydrogen atom and a negatively-charged atom.

Hydrogen bonding does not occur in molecules with nonpolar covalent bonds. Any compound with polar covalent bonds has the potential to form hydrogen bonds.

Hydrogen bonds account for some important qualities of water:

- water remains liquid over a wide temperature range;
- water has an unusually high heat of vaporization.
- water has a much higher boiling point than other hydrides.

Hydrogen bonding is most significant between hydrogen and highly electronegative atoms. The length of the chemical bond depends upon its strength, pressure, and temperature. The bond angle depends on the specific chemical species involved in the bond. The strength of hydrogen bonds ranges from very weak to very strong.

### REVISION EXERCISES

#### **Ex. 1. Answer the following questions.**

1. What is a chemical bond caused by?
2. What is bond energy?
3. What are the principal types of a chemical bond?
4. When is an ionic bond formed?
5. How is the polarity of a covalent bond defined?
6. What bond is responsible for the crystalline structure of pure metals?
7. What is the reason of hydrogen bonding?

#### **Ex. 2. Match the words with their definitions.**

- |                  |  |
|------------------|--|
| 1) attraction    | a) a measure of the combining power of an element with other atoms when it forms chemical compounds or molecules   |
| 2) charge        | b) a positively charged ion that is attracted to the cathode in electrolysis   |
| 3) valence       | c) a protein that functions as a catalyst for a chemical reaction  |
| 4) cation        | d) the physical property of matter that causes it to experience a force when placed in an electromagnetic field  |
| 5) bonding       | e) a system that uses only two values (as 0 and 1 or yes and no) to represent codes and data   |
| 6) binary system | f) the force attracting atoms to each other and binding them together in a molecule  |
| 7) enzyme        | g) an interaction that accounts for the association of atoms into molecules, ions, crystals and other stable species that make up the familiar substance |

#### **Ex. 3. Say whether the following statements are true or false.**

1. A chemical bond is a region that forms when electrons from different atoms interact with each other.
2. The bond is caused by the elec-

electrostatic force of attraction between similar charges. 3. The negatively charged electrons orbiting the nucleus and the positively charged protons in the nucleus repel each other. 4. The atoms in molecules, crystals, metals are held together by chemical bonds which dictate the properties of matter. 5. Covalent bonds are created between atoms where one is a metal and one is a non-metal element. 6. The polarity of a covalent bond is defined by any difference in electropositivity. 7. A coordinate covalent bond is formed when one atom donates both of the electrons to form a single covalent bond. 8. Metallic bond is the strongest of the three major bonds because the electrons are shared in more than just the first shells.

**Ex. 4. Insert the necessary word.**

1. The extreme mobility of the electrons in a metal explains its high thermal and electrical ... . 2. Hydrogen bonding does not occur in molecules with nonpolar ... bonds. 3. Chemical bonds allow all of the elements to ... in a variety of ways to create everything on the Earth. 4. Covalent bonds are of practical importance in ... chemistry because of the ability of the carbon atom to form four covalent bonds. 5. ... covalent bonds are common for certain atoms depending upon their valence configuration. 6. An ionic bond can occur at the centre of a large covalently bonded organic molecule such as ... . 7. All bonds arise from the ... of unlike charges.

multiple, combine, attraction, conductivity, enzyme, covalent, organic

# UNIT IV

## ISOMERISM

Isomerism is the phenomenon when certain compounds, with the same molecular formula, exist in different forms owing to their different organizations of atoms. The concept of isomerism illustrates the fundamental importance of molecular structure and shape in organic chemistry.

The molecular formula of organic compounds tells you how many atoms of each element are present in a molecule. The different structures lead to different properties.

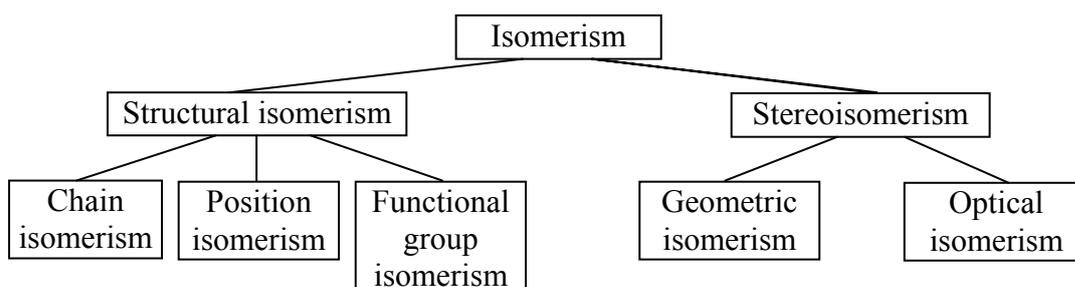
Two molecules that have the same molecular formula but differ in the way atoms are arranged are called isomers.

Isomers are distinct compounds with different physical properties and often different chemical properties too. The occurrence of isomers (isomerism) is very common in carbon compounds because of the great variety of ways in which atoms carbon can form chains and rings, but you will meet examples in inorganic chemistry too.

The atoms are bonded together in a different order in each isomer. These are called structural isomers.

The order of bonding in the isomer is the same; but the arrangement of atoms in space is different in each isomer. These are called stereoisomers.

### The isomerism tree



**Structural isomerism.** “Structural” isomers are widely called “conformational” isomers. The latter term is preferred in the IUPAC system of nomenclature. Structural isomerism occurs when two or more organic compounds have the same molecular formulae, but different structures. These differences tend to give the molecules different chemical and physical properties. There are three types of structural isomerism that you need to be aware of: chain isomerism, positional

isomerism and functional isomerism. There is a fourth type, known as tautomerism (where there are two isomers known as the keto and enol isomers) that will not be introduced here.

*Chain isomerism* occurs when the way carbon atoms are linked together is different from compound to compound. It is also called nuclear isomerism. Carbon chains can be straight or branched. Butane and methylpropane are examples of chain isomerism.

There are three chain isomers of  $C_5H_{12}$  shown below. Note that these isomers have the same empirical formula as pentane, but different conformations.

*Position isomerism* can occur when molecule with one (or more) functional groups are situated in different positions on the same carbon chain in the molecule. For example, there are two isomeric compounds with the molecular formula  $C_3H_7Cl$ . The  $-Cl$  functional group is situated at two different places on the hydrocarbon chain. Positional isomers of alcohols, alkenes, and aromatics are common.

*Functional group isomerism.* It is sometimes possible for compounds with the same molecular formula to have different functional groups. As well as showing different physical properties (such as boiling point), they have quite different chemical properties because they belong to different homologous series. There are two functional group isomers of which you need to be aware:

- alcohols and ethers;
- aldehydes and ketones.

***Stereoisomerism.*** Stereoisomers have identical molecular formula and the atoms are held together in the same order, but the arrangement of atoms in space is different in each isomer. Stereoisomers may possess quite different physical properties, such as melting point, density and solubility in water (e. g. maleic acid and fumaric acid). Ring structures and other steric factors also result in geometric isomerism. They have different spatial arrangements and their molecules are not superimposable. There are two different ways this can happen: geometric isomerism and optical isomerism.

*Geometric isomerism* can occur in compounds that contain a  $C=C$  double bond. That does not allow free rotation about the double bond (unlike a  $C-C$  single bond). They are not superimposable. For example, there are two isomers of 1,2-dichloroethane ( $C_2H_2Cl_2$ ) depending on whether the chlorine atoms are on the same, or opposite sides of the double bond. They are called *cis*- and *trans*- isomer respectively.

*Optical isomerism* occurs when a molecule is asymmetric, i. e. it does not have a center or plane of symmetry. Optical isomerism involves an atom, usually carbon, bonded to four different atoms or groups of atoms. They exist in pairs. It means that there will be two different forms of the molecule that are mirror images of each other – rather like your right and left hand. Such compounds are called optical isomers or enantiomers. The central carbon atom, to which four different atoms or groups are attached, is called an asymmetrical carbon atom. Enantiomers have identical physical constants, such as melting points and boiling points, but are said to be optically active since they can be distinguished from each other by their ability to rotate the plane of polarised light in opposite directions. A mixture of enantiomers in equal proportions is optically inactive, and is called a racemic mixture. The isomers are often labeled D- or compounds too, particularly in the complexes of transition-metal ions with ligands.

Other types of isomerism exist outside this scope. Topological isomers called topoisomers are generally large molecules that wind about and form different shaped knots or loops. Molecules with topoisomers include catenanes and DNA. Topoisomerase enzymes can knot DNA and thus change its topology. There are also isotopomers or isotopic isomers that have the same numbers of each type of isotopic substitution but in chemically different positions. In nuclear physics, nuclear isomers are excited states of atomic nuclei.

## REVISION EXERCISES

### Ex. 1. Answer the following questions.

1. What is the phenomenon of isomerism? 2. How are isomers classified according to the order of atoms or their arrangement in space? 3. Describe the isomerism tree. 4. Characterize each type of isomerism. 5. When are isomers super imposable? 6. What discoveries were made by Wöhler and Pasteur to prove isomerism? 7. Who introduced the term isomerism?

### Ex. 2. Match the words with their definitions.

- |                |   |
|----------------|---|
| 1) occur       | a) to cause (two or more people or things) stop being together, joined or connected |
| 2) arrangement | b) to connect, to combine, to unite   |
| 3) introduce   | c) the act or process of moving or turning around a central point                   |

- |               |  |
|---------------|--|
| 4) link       | d) the amount of a substance that will dissolve in a given amount of another substance |
| 5) separate   | e) to cause something to begin to be used for the first time                           |
| 6) solubility | f) to happen, to be found or met with  |
| 7) rotation   | g) the way that things are organized for a particular purpose or activity              |

**Ex. 3. Say whether the following statements are true or false.**

1. Topological isomers called topoisomers are generally large molecules that wind about and form different shaped knots or loops. 2. Geometric isomers are superimposable. 3. The central carbon atom, to which four different atoms or groups are attached, is called an asymmetrical carbon atom. 4. Chain isomerism occurs when the way carbon atoms are linked together is the same. 5. Two molecules that have the same molecular formula but differ in the way atoms are arranged are called asymmetrical molecules. 6. There are three types of structural isomerism: chain isomerism, positional isomerism and functional isomerism.

**Ex. 4. Insert the necessary word.**

1. The roots of the word isomer are Greek – isos plus meros, or “equal parts.” Stated colloquially, isomers are chemical ... that have the same parts but are nonetheless not the same. 2. To make a crude analogy, two bracelets, each consisting of five red and five green beads, could be ... in many different isomeric forms, depending on the order of the colours. 3. Each bracelet would have the same parts – that is, the five red and five green beads – but each ... would be different. 4. One could also imagine ... of those same beads in which pendant chains were attached to a bracelet in a variety of ways. 5. One might imagine two bracelets of the same red-green order but with ... chains attached in different orientations. Such structures also would be analogous to isomers. 6. In a more subtle ..., one’s hands can be seen as isomeric. 7. Each hand possesses the same kinds of fingers, but a right ... can never be superimposed perfectly on a left hand; they are different.

identical, variation, hand, arranged, combinations, compounds, analogy
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**Ex. 5. Translate the following text.****History of isomerism**

Isomerism was first noticed in 1827, when Friedrich Wöhler prepared cyanic acid and noted that although the elemental composition was identical to fulminic acid (prepared by Justus von Liebig the previous year), its properties were quite different. This finding challenged the prevailing chemical understanding of the time, which held that chemical compounds could be different only when they had different elemental compositions. After additional discoveries of the same sort were made, such as Wöhler's 1828 discovery that urea had the same atomic composition as the chemically distinct ammonium cyanate, Jöns Jakob Berzelius introduced the term isomerism to describe the phenomenon.

In 1849, Louis Pasteur separated tiny crystals of tartaric acid into their two mirror-image forms. The individual molecules of each were the left and right optical stereoisomers, solutions of which rotate the plane of polarized light in opposite directions.

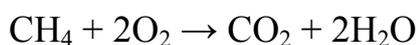
# UNIT V

## HYDROCARBONS

**Simple Hydrocarbons.** The simplest hydrocarbons are those that contain only carbon and hydrogen. These simple hydrocarbons come in three varieties depending on the type of carbon-carbon bonds that occur in the molecule. *Alkanes* are the first class of simple hydrocarbons and contain only carbon-carbon single bonds. The alkanes are named by combining a prefix that describes the number of carbon atoms in the molecule with the root ending *-ane*. The names and prefixes for the first ten alkanes are given in the following list.

1. Meth- Methane  $\text{CH}_4$   $\text{CH}_4$
2. Eth- Ethane  $\text{C}_2\text{H}_6$   $\text{CH}_3\text{CH}_3$
3. Prop- Propane  $\text{C}_3\text{H}_8$   $\text{CH}_3\text{CH}_2\text{CH}_3$
4. But- Butane  $\text{C}_4\text{H}_{10}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
5. Pent- Pentane  $\text{C}_5\text{H}_{12}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
6. Hex- Hexane  $\text{C}_6\text{H}_{14}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
7. Hept- Heptane  $\text{C}_7\text{H}_{16}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
8. Oct- Octane  $\text{C}_8\text{H}_{18}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
9. Non- Nonane  $\text{C}_9\text{H}_{20}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
10. Dec- Decane  $\text{C}_{10}\text{H}_{22}$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

The chemical formula for any alkane is given by the expression  $\text{C}_n\text{H}_{2n+2}$ . The structural formula, shown for the first five alkanes in the table, shows each carbon atom and the elements that are attached to it. This structural formula is important when we begin to discuss more complex hydrocarbons. The simple alkanes share many properties in common. All enter into combustion reactions with oxygen to produce carbon dioxide and water vapour. In other words, many alkanes are flammable. This makes them good fuels. For example, methane is the principle component of natural gas, and butane is common lighter fluid:



**The combustion of methane.** The second class of simple hydrocarbons, the *alkenes*, consists of molecules that contain at least one double-bonded carbon pair. Alkenes follow the same naming convention used for alkanes. A prefix (to describe the number of carbon atoms) is combined with the ending *-ene* to denote an alkene. Ethene, for example is the two-carbon molecule that contains one double bond. The chemical formula for the simple alkenes follows the expression

$C_nH_{2n}$ . Because one of the carbon pairs is double bonded, simple alkenes have two fewer hydrogen atoms than alkanes. *Alkynes* are the third class of simple hydrocarbons and are molecules that contain at least one triple-bonded carbon pair. Like the alkanes and alkenes, alkynes are named by combining a prefix with the ending *-yne* to denote the triple bond. The chemical formula for the simple alkynes follows the expression  $C_nH_{2n-2}$ , e. g. ethyne.

**Hydrocarbons.** These are compounds composed of carbon and hydrogen. They are generally insoluble in water although those with lighter molecular masses are gases and are slightly soluble. Examples of hydrocarbons include methane – the gas we burn as natural gas, propane (also called liquid petroleum gas) and petroleum jelly.

The carbon atoms join together to form the framework of the compound; the hydrogen atoms attach to them in many different configurations. Hydrocarbons are the principal constituents of petroleum and natural gas. They serve as fuels and lubricants as well as raw materials for the production of plastics, fibers, rubbers, solvents, explosives, and industrial chemicals.

Many hydrocarbons occur in nature. In addition to making up fossil fuels, they are present in trees and plants, as, for example, in the form of pigments called carotenes that occur in carrots and green leaves. More than 98 percent of natural crude rubber is a hydrocarbon polymer, a chainlike molecule consisting of many units linked together. The structures and chemistry of individual hydrocarbons depend in large part on the types of chemical bonds that link together the atoms of their constituent molecules.

Nineteenth-century chemists classified hydrocarbons as either aliphatic or aromatic on the basis of their sources and properties. Aliphatic (from Greek *aleiphar*, “fat”) described hydrocarbons derived by chemical degradation of fats or oils. Aromatic hydrocarbons constituted a group of related substances obtained by chemical degradation of certain pleasant-smelling plant extracts. The terms aliphatic and aromatic are retained in modern terminology, but the compounds they describe are distinguished on the basis of structure rather than origin.

Aliphatic hydrocarbons are divided into three main groups according to the types of bonds they contain: alkanes, alkenes, and alkynes. Alkanes have only single bonds, alkenes contain a carbon-carbon double bond, and alkynes contain a carbon-carbon triple bond. Aromatic hydrocarbons are those that are significantly more stable than their

Lewis structures would suggest; i. e. they possess “special stability”. They are classified as either arenes, which contain a benzene ring as a structural unit, or non-benzenoid aromatic hydrocarbons, which possess special stability but lack a benzene ring as a structural unit.

This classification of hydrocarbons serves as an aid in associating structural features with properties but does not require that a particular substance be assigned to a single class. Indeed, it is common for a molecule to incorporate structural unit characteristic of two or more hydrocarbon families. A molecule that contains both a carbon-carbon triple bond and a benzene ring, for example, would exhibit some properties that are characteristic of alkynes and others that are characteristic of arenes.

### Hydrocarbons classification

Hydrocarbons and compounds derived from them generally fall into three large categories.

*Aliphatic hydrocarbons* consist of chain of carbon atoms that do not involve cyclic structures. They are often referred to as open-chain or acyclic structures, e. g. propane, pentane, hexane.

*Alicyclic or simply cyclic hydrocarbons* are composed of carbon atoms arranged in a ring or rings, e. g. cyclopropane, cyclopentane, cyclohexane.

*Aromatic hydrocarbons* are a special group of cyclic compounds that usually have six-membered rings with alternative single and double bonds. They are classed separately from aliphatic and alicyclic hydrocarbons because of their characteristic physical and chemical properties, e. g. benzene, naphthalene.

*Addition of hydrogen (hydrogenation)* to a carbon-carbon double bond, reduces an alkene to an alkane. The process requires the presence of a metal catalyst, and for this reason, it is also called catalytic reduction. Catalytic reduction of alkenes is a very important reaction in the laboratory. In hydrogenation, both hydrogen atoms are added to the same side of the alkene molecule.

*The addition of water to an alkene* is called hydration. In the presence of an acid catalyst, often 60% aqueous sulfuric acid, water adds to alkenes to produce alcohols. Hydrogen adds to the carbon of the double bond with the greater number of hydrogen; OH adds to alkenes in accordance with Markovnikov’s rule. Hydration of alkenes is a very important reaction both in the chemical industry and in biological systems.

**Sources and uses of hydrocarbons.** Petroleum and its associated natural gases are now the major source of hydrocarbons. Natural gas is composed principally of methane ( $\text{CH}_4$ ). Ethane ( $\text{C}_2\text{H}_6$ ) and propane ( $\text{C}_3\text{H}_8$ ) typically represent 5 to 10 per cent of the total, along with traces of  $\text{C}_4$  and  $\text{C}_5$  hydrocarbons. The gas is freed of various unwanted contaminants and then it is utilized almost exclusively as fuel. Valuable side products of petroleum cracking provide raw materials for the petrochemical industry. Ethylene ( $\text{C}_2\text{H}_4$ ) and propylene ( $\text{C}_3\text{H}_6$ ) are principal starting points for the manufacture of chemicals, medicines, and polymers.

### REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. What are naturally occurring hydrocarbons? 2. What classifications are hydrocarbons divided into? 3. What purposes do the classifications serve to? 4. What are hydrocarbons composed of? 5. What are alkanes? Give examples. 6. What is the chemical formula of alkanes? 7. What are the chemical reactions of alkanes? 8. What are the three classes of hydrocarbons? 9. What are the rules of naming them? 10. What other classifications are hydrocarbons divided into? 11. What is hydrogenation? 12. Why is hydrogenation called catalytic reduction? 13. What is hydration? 14. What are sources and uses of hydrocarbons?

#### Ex. 2. Match the words with their definitions.

- |             |  |
|-------------|--|
| 1) liquid   | a) a material (such as coal, oil, or gas) that is burned to produce power  |
| 2) medicine | b) to cause to combine until there is no further tendency to combine   |
| 3) fuel     | c) a special part or characteristic, quality, structure, form  |
| 4) bond     | d) a substance that is used in treating disease or relieving pain, and that is usually in the form of a pill or liquid |
| 5) feature  | e) capable of flowing freely like water: not a gas or a solid  |
| 6) saturate | f) an attractive force that holds together atoms, ions, or groups of atoms in a molecule or crystal                    |

#### Ex. 3. Say whether the following statements are true or false.

1. The structures and chemistry of individual hydrocarbons do not depend in large part on the types of chemical bonds that link together the atoms of their constituent molecules. 2. The addition of hydrogen to

an alkene is called hydration. 3. Petroleum and its associated natural gases are now the major source of hydrocarbons. 4. The addition of hydrogen to a carbon-carbon double bond, called hydrogenation, reduces an alkene to an alkane. 5. Aromatic hydrocarbons are a special group of cyclic compounds that usually have six-membered rings with alternative triple and double bonds. 6. Aliphatic hydrocarbons are divided into three main groups according to the types of bonds they contain: alkanes, alkenes, and alkynes.

**Ex. 4. Insert the necessary word.**

1. Alkanes are described as saturated hydrocarbons, while ..., alkynes, and aromatic hydrocarbons are said to be unsaturated. 2. Hydrocarbons with single carbon-carbon bonds are referred to as being ... whilst any hydrocarbon that contains a double bond is said to be ... . 3. Saturated hydrocarbons are also called the ..., while the unsaturated hydrocarbons include both those molecules that contain carbon-carbon double bonds (referred to as the alkenes) and those that contain carbon-carbon triple bonds (referred to as the ...). 4. ... and ... are natural products that have resulted from the ... of organic compounds from plants and animals that lived millions of years ago. 5. They are found today as petroleum, which are ... of hydrocarbons containing up to 30 or 40 carbon atoms. 6. Different components of ... can be isolated by fractional distillation. 7. These hydrocarbons are good sources of fuels, the so-called "fossil fuels". 8. As mentioned previously, the global production of such fossil fuels is 3 billion tonnes. 9. As they are produced in such large quantities, ... of the environment with these fossil fuels is of concern. 10. The major route of entry into the environment isn't through spectacular ... such as the oil spills from ships, but rather through our daily activities. 11. Pumping fuel into cars, and oil spilled onto the road as a result of old faulty cars are major contributors.

disasters, alkanes (×2), mixtures, decay, saturated, alkynes, pollution, alkenes (×2), petroleum, unsaturated
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# UNIT VI

## ALKANES, ALKENES, ALKYNES

### Alkanes

A chain of carbon atoms that contains the maximum number of hydrogen atoms has the general formula  $C_nH_{2n+2}$  ( $n$  – number of carbon atoms). This type of hydrocarbon is called an alkane (a historical name is paraffin). Alkanes are saturated hydrocarbons, they consist only of carbon and hydrogen atoms and all bonds are single bonds. The simplest possible alkane is methane  $CH_4$ . Alkanes can exist in straight chains, chains with branching, and cycles. The carbon atom in an alkane forms four single bonds that are equidistant from each other. The shape is referred to as tetrahedral. There is no limit to the number of carbon atoms that can be linked together, the only limitation being that the molecule is acyclic, is saturated and is a hydrocarbon. When the carbon atoms of an alkane are connected in a single continuous sequence, the alkane is known as a normal hydrocarbon. These alkanes are sometimes called linear or straight-chain hydrocarbons, but the names are misleading. Really, the carbon chains are kinked, twisted and are linear only in symbolic representations. A succession of normal hydrocarbons which differ by one methylene ( $-CH_2-$ ) group is known as homologous series. Alkanes belong to a homologous series of organic compounds in which the members differ by a molecular mass. Alkanes with more than three carbon atoms can be arranged in various different ways, forming structural isomers. The simplest isomer of an alkane is the one in which the carbon atoms are arranged in a single chain with no branches. This isomer is sometimes called the  $n$ -isomer ( $n$  for “normal”, although it is not necessarily the most common). However the chain of carbon atoms may also be branched at one or more points. The number of possible isomers increases rapidly with the number of carbon atoms.

The two major sources of alkanes are natural gas and petroleum. Natural gas consists of approximately 90 to 95% methane, 5 to 10% ethane, and a mixture of other relatively low-boiling alkanes (propane, butane and 2-methylpropane). Petroleum is a thick, viscous, liquid mixture of thousands of compounds, most of them hydrocarbons, formed by the decomposition of marine plants and animals.

Knowledge about the names of alkanes is extremely important because the names of alkanes form the basis for the names of many other

types of organic compounds. The trivial (non-systematic) name for alkanes is *paraffins*. Together, alkanes are known as the *paraffin series*. A system of nomenclature for organic compounds has been developed by the International Union of Pure and Applied Chemistry (IUPAC). The IUPAC name for an alkane consists of two parts: a prefix that shows the number of carbon atoms and the suffix *-ane*. The names of the first ten alkanes are:  $\text{CH}_4$  – methane,  $\text{CH}_3\text{CH}_3$  – ethane,  $\text{CH}_3\text{CH}_2\text{CH}_3$  – propane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  – butane,  $\text{C}_5\text{H}_{12}$  – pentane,  $\text{C}_6\text{H}_{14}$  – hexane,  $\text{C}_7\text{H}_{16}$  – heptane,  $\text{C}_8\text{H}_{18}$  – octane,  $\text{C}_9\text{H}_{20}$  – nonane,  $\text{C}_{10}\text{H}_{22}$  – decane.

**Physical Properties.** The first four alkanes ( $\text{C}_1$  to  $\text{C}_4$ ) are all gases at room temperature. Natural gas is mostly methane. Compounds from  $\text{C}_5$  to  $\text{C}_{17}$  are oily liquids. Petroleum contains a wide variety of alkanes. Natural gas and petroleum alkanes are used mainly for fuels. Compounds greater than  $\text{C}_{17}$  are solids at room temperature and pressure. They are nonpolar compounds. The only interactions between their molecules are the very weak London dispersion forces. They have the low boiling points and the low melting points. As the number of carbon atoms increases, the molecules become larger and heavier. This means that their melting points and boiling points increase. In general, both boiling and melting points of alkanes decrease with increasing the number of branches (for alkanes with the same molecular weights). Alkanes are insoluble in water, but they are soluble in non-polar solvents such as toluene and tetrachloromethane. Their density usually increases with increasing number of carbon atoms but is less than that of water. The melting points of branched-chain alkanes can be either higher or lower than those of the corresponding straight-chain alkanes, again depending on the ability of the alkane in question to pack well in the solid phase. Alkanes do not conduct electricity, nor are they substantially polarized by an electric field. All alkanes are colourless and odourless.

**Chemical properties.** Alkanes are relatively inert. Most reactions require specialized catalysts for breaking the carbon-carbon bonds. Although they are relatively unreactive, alkanes do undergo two important kinds of reactions: reactions with oxygen (combustion) and substitution of hydrogen atoms with chlorine and other halogens (halogenation). Burning, oxidation of alkanes, is a very important reaction in using alkanes as fuel. The fuels used in engines require additives to improve the combustibility for smooth and efficient burning. In burning, the alkanes react with the oxygen in air to produce carbon dioxide and water. Methane and other alkanes react with chlorine in sunlight or at

high temperature in a substitution reaction. The reaction of an alkane with other halogens (such as bromine) results in a range of substitution products called haloalkanes. Alkanes are useful as solvents for a wide range of organic substances.

## Alkenes

Alkene is an unsaturated hydrocarbon that contains one or more carbon-carbon double bonds. The compounds are said to be unsaturated because they do not have the maximum number of atoms each carbon is able to accommodate. The molecular formula of this group is  $C_nH_{2n}$  ( $n$  is the number of carbon atoms). Alkenes have less hydrogen atoms than alkanes. Ethene (or ethylene as it is sometimes called) is the simplest alkene. Alkenes are often referred to as olefins, an old term derived from the fact that chlorine adds to gaseous ethylene to form an oily product.

Naming alkenes, we replace the suffix *-ane* of the corresponding alkane by *-ene*.

*Physical properties* of alkenes are similar to those of alkanes with the same carbon skeletons. The low-molecular-weight alkenes of importance in the petrochemical industry are gases. Most common alkenes found in the chemical laboratory are pungent-smelling liquids. Like alkanes, alkenes are relatively nonpolar compounds which are insoluble in water.

The alkenes are generally more reactive than the alkanes. The carbon-carbon double bond is an unsaturated linkage to which many chemical reagents can add. Chlorination and hydrogenation are two of the addition reactions that are typical of alkenes. The reaction of ethene with bromine is a simple example of an addition reaction. An example of hydrogenation is the reaction of propylene with hydrogen. Alkenes also undergo combustion reactions. For example, propene burns in a supply of air to give carbon dioxide and water. If there is not enough oxygen available, propene will burn with a yellow flame and produce soot (carbon) and carbon monoxide (CO).

An alkene that contains two double bonds is called a diene. If the two double bonds are separated by only one single bond, such as in 1,3-butadiene, the double bonds are said to be in conjugation.

Alkenes may be oxidized to ketones or carboxylic acids by an oxidizing agent. If the carbon in the double bond is attached to two alkyl groups, a ketone is the product. If the carbon has only one alkyl group, a carboxylic acid is the product.

Ethene (ethylene) and propene (propylene) are present in small quantities in natural gas and petroleum. The chemical industry prepares enormous quantities of these compounds by heating ethane and propane. Ethylene and propylene are used to manufacture plastics and a number of organic chemicals, including ethanol (alcohol), acetic acid, and ethylene glycol (antifreeze).

## Alkynes

Alkynes are unsaturated hydrocarbons which contain one or more carbon-carbon triple bonds. The molecular formula of this group is  $C_nH_{2n-2}$  ( $n$  is the number of carbon atoms). Alkynes have less hydrogen atoms than alkanes and alkenes. Alkynes are more unsaturated than alkenes. The simplest alkyne is ethyne (or acetylene ( $C_2H_2$ )) as it is sometimes called) Alkynes are often referred to as acetylenes, a non IUPAC name (International Union of Pure and Applied Chemistry). They show greater tendency to polymerize or oligomerize than alkenes do. The resulting polymers, called polyacetylenes (which do not contain alkyne units) are conjugated and can exhibit semiconducting properties. Naming unbranched alkynes, we replace the suffix *-ane* of alkanes by *-yne*.

The *physical properties* of alkynes are similar to those of alkenes and alkanes. These unsaturated compounds undergo additions similar to alkenes. Hydrogenation of alkynes produces alkanes and alkenes.

Acetylene, the dominant alkyne, is used as a fuel and a precursor to other compounds, e. g., acrylates. Hundreds of millions of kilograms are produced annually by partial oxidation of natural gas. Acetylene is widely used in the oxy-acetylene welding torch because it burns in oxygen with a hot flame. Ethyne (trivial name acetylene) burns in air with a luminous flame and produces a lot of soot. If a good supply of oxygen is available, ethyne burns with a colourless flame. Propyne, also industrially useful, is also prepared by thermal cracking of hydrocarbons. Most other industrially useful alkyne derivatives are prepared from acetylene, e. g. via condensation with formaldehyde.

Specialty alkynes are prepared by dehydrohalogenation of vicinal alkyl dihalides or vinyl halides. Via the Fritsch – Buttenberg – Wiechell rearrangement, alkynes are prepared from vinyl bromides. Alkynes can be prepared from aldehydes using the Corey – Fuchs reaction and from aldehydes or ketones by the Seyferth – Gilbert homologation. In the alkyne zipper reaction, alkynes are generated from other alkynes by treatment with a strong base.

Halogenation of alkynes gives the vinyl dihalides or alkyl tetrahalides. The hydroboration of alkynes gives vinylic boranes which oxidize to the corresponding aldehyde or ketone. Hydrohalogenation gives the corresponding vinyl halides or alkyl dihalides, again depending on the number of HX added.

## REVISION EXERCISES

### Ex. 1. Answer the following questions.

1. What is a normal hydrocarbon? 2. In what physical states do alkanes exist? 3. Where are alkanes soluble? 4. What is a non IUPAC name of alkenes? 5. How is an alkene with two double bonds called? 6. How are alkynes prepared? 7. What does hydrogenation of alkynes result in?

### Ex. 2. Match the words with their definitions.

- |                          |   |
|--------------------------|---|
| 1) saturated hydrocarbon | a) a chemical reaction that involves the reaction of a compound with halogen and results in the halogen added to the compound                                     |
| 2) sequence              | b) a chemical compound or substance that may speed up or slow down a chemical reaction without itself being changed or consumed at any time during the reaction   |
| 3) isomer                | c) the simplest hydrocarbon species which is composed entirely of single bonds  |
| 4) catalyst              | d) an ordered collection of elements in which repetitions are allowed   |
| 5) halogenation          | e) any chemical reaction that involves the moving of electrons  |
| 6) combustion            | f) a high-temperature exothermic redox chemical reaction between a fuel and an oxidant, usually atmospheric oxygen  |
| 7) oxidation             | g) one of two or more compounds, radicals, or ions that contain the same number of atoms of the same elements but differ in structural arrangement and properties |

### Ex. 3. Say whether the following statements are true or false.

1. Alkanes are unsaturated hydrocarbons as they consist of carbon and hydrogen atoms and all bonds are double bonds. 2. The alkanes are

sometimes called linear hydrocarbons because the carbon chains are straight. 3. Boiling and melting points of alkanes with the same molecular weights decrease with increasing the number of branches. 4. Most common alkenes found in the chemical laboratory are pungent-smelling liquids. 5. Alkenes may be oxidized to ketones if the carbon in the double bond is attached to two alkyl groups. 6. Alkynes are often referred to as olefins, a non IUPAC name. 7. Alkynes are unsaturated hydrocarbons which contain one or more carbon-hydrogen triple bonds.

**Ex. 4. Insert the necessary word.**

1. The carbon atom in an ... forms four single bonds that are equidistant from each other. 2. The ... of alkanes increases with increasing the number of carbon atoms but is less than that of water. 3. Most reactions of alkanes require specialized ... for breaking the carbon-carbon bonds. 4. Chlorination and hydrogenation are two of the ... reactions that are typical of alkenes. 5. The low-molecular-weight alkenes of importance in the petrochemical industry are ... . 6. The parent ... of alkynes must include the triple bond even if it is not the longest possible carbon chain in the molecule. 7. ... of alkynes produces alkanes and alkenes.

gases, density, hydrogenation, alkane, chain, catalysts, addition

## UNIT VII

# HALOGENS AND THEIR DERIVATIVES

The halogens are the family of chemical elements that includes fluorine (atomic symbol F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Chlorine was the first halogen to be discovered in 1774, followed by iodine, bromine, fluorine, and astatine was discovered last in 1940. The halogens make up Group VIIA of the Periodic Table of the elements. Elemental halogens are diatomic molecules. The bonds in these diatomic molecules are non-polar covalent single bonds. Due to their high reactivity, the halogens are never found in nature in native form. Compounds containing more than one kind of halogen are possible. As a general rule, fluorine is the most reactive halogen and astatine is the least reactive. The name “halogen” is derived from the Greek roots hal- (“salt”) and -gen (“to form”). Together these words combine to mean “salt former”, referencing the fact that halogens form salts when they react with metals. The salinity of the oceans on Earth is due in large part to such halogen salts (halides) as sodium chloride (NaCl) and potassium iodide (KI).

Halogens display physical and chemical properties typical of non-metals. They have relatively low melting and boiling points that increase steadily down the group. At room temperature, the halogens demonstrate all of the physical states: fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. All of the elements are colored, with the color becoming more intense moving down the group. Fluorine gas is pale yellow, and chlorine gas is a yellowish green. Liquid bromine and its vapors are brownish red. Solid iodine appears as shiny, dark gray crystals, and the vapors are a deep purple. The halogens are poor thermal and electrical conductors in all phases, and as solids they are brittle and crumbly. The halogens have distinctive, unpleasant odors, and are toxic.

The neutral atoms of the halogens possess seven outer electrons, they only require one additional electron to form a full octet. This characteristic makes them more reactive than other non-metal groups. An additional electron can be added to halogen atoms to form singly charged negative ions. These ions have a closed outer-shell configuration. Electronegativity is a measure of the ability of an atom of one element to remove an electron from an atom of another element. As a group, the halogens are among the most electronegative elements. Flu-

orine has the highest electronegativity of all the elements. Halogens are so reactive that all the elements except helium and neon have been found to react with at least one of the halogens.

## Elements

**Fluorine.** Fluorine has an atomic number of 9 and is denoted by the symbol F. Elemental fluorine was first discovered in 1886 by isolating it from hydrofluoric acid. Fluorine exists as a diatomic molecule in its free state ( $F_2$ ) and is the most abundant halogen found in the Earth's crust. Fluorine is the most electronegative element in the periodic table. It appears as a pale yellow gas at room temperature. Fluorine also has a relatively small atomic radius. Its oxidation state is always  $-1$  except in its elemental, diatomic state (in which its oxidation state is zero). Fluorine is extremely reactive and reacts directly with all elements except helium (He), neon (Ne) and argon (Ar). In  $H_2O$  solution, hydrofluoric acid (HF) is a weak acid. Although fluorine is highly electronegative, its electronegativity does not determine its acidity; HF is a weak acid due to the fact that the fluoride ion is basic ( $pH > 7$ ). In addition, fluorine produces very powerful oxidants. For example, fluorine can react with the noble gas xenon and form the strong oxidizing agent Xenon Difluoride ( $XeF_2$ ).

**Chlorine.** Chlorine has the atomic number 17 and the chemical symbol Cl. Chlorine was discovered in 1774 by extracting it from hydrochloric acid. In its elemental state, it forms the diatomic molecule  $Cl_2$ . Chlorine exhibits multiple oxidation states, such as  $-1$ ,  $+1$ ,  $3$ ,  $5$ , and  $7$ . At room temperature it appears as a light green gas. Since the bond that forms between the two chlorine atoms is weak, the  $Cl_2$  molecule is very reactive. Chlorine reacts with metals to produce salts called chlorides. Chloride ions are the most abundant ions that dissolve in the ocean. Chlorine also has two isotopes:  $^{35}Cl$  and  $^{37}Cl$ . Sodium chloride is the most prevalent compound of the chlorides.

**Bromine.** Bromine has an atomic number of 35 with a symbol of Br. It was first discovered in 1826. In its elemental form, it is the diatomic molecule  $Br_2$ . At room temperature, bromine is a reddish-brown liquid. Its oxidation states vary from  $-1$ ,  $+1$ ,  $3$ ,  $4$ , and  $5$ . Bromine is more reactive than iodine, but not as reactive as chlorine. Also, bromine has two isotopes:  $^{79}Br$  and  $^{81}Br$ . Bromine consists of bromide salts, which have been found in the sea. The world production of bromide has increased significantly over the years, due to its access and

longer existence. Like all of the other halogens, bromine is an oxidizing agent, and is very toxic.

**Iodine.** Iodine has the atomic number 53 and symbol I. Iodine has oxidation states  $-1$ ,  $+1$ ,  $5$ , and  $7$ . Iodine exists as a diatomic molecule,  $I_2$ , in its elemental state. At room temperature, it appears as a violet solid. Iodine has one stable isotope:  $^{127}I$ . It was first discovered in 1811 through the use of seaweed and sulfuric acid. Currently, iodide ions can be isolated in seawater. Although iodine is not very soluble in water, the solubility may increase if particular iodides are mixed in the solution. Iodine has many important roles in life, including thyroid hormone production.

**Astatine.** Astatine is a radioactive element with an atomic number of 85 and symbol At. Its possible oxidation states include:  $-1$ ,  $+1$ ,  $3$ ,  $5$ , and  $7$ . It is the only halogen that is not a diatomic molecule and it appears as a black, metallic solid at room temperature. Astatine is a very rare element, so there is not much known about this element. In addition, astatine has a very short radioactive half-life, no longer than a couple of hours. It was discovered in 1940 by synthesis. Also, it is thought that astatine is similar to iodine. However, these two elements are assumed to differ by their metallic character.

### Applications of halogens

**Fluorine.** Although fluorine is very reactive, it serves many industrial purposes. For example, it is a key component of the plastic polytetrafluoroethylene (called Teflon-TFE by the DuPont company) and certain other polymers, often referred to as fluoropolymers. Chlorofluorocarbons (CFCs) are organic chemicals that were used as refrigerants and propellants in aerosols before growing concerns about their possible environmental impact led to their discontinued use. Hydrochlorofluorocarbons (HFCs) are now used instead. Fluoride is also added to toothpaste and drinking water to help reduce tooth decay. Fluorine also exists in the clay used in some ceramics. Fluorine is associated with generating nuclear power as well. In addition, it is used to produce fluoroquinolones, which are antibiotics.

**Chlorine.** Chlorine has many industrial uses. It is used to disinfect drinking water and swimming pools. Sodium hypochlorite ( $NaClO$ ) is the main component of bleach. Hydrochloric acid, sometimes called muriatic acid, is a commonly used acid in industry and laboratories. Chlorine is also present in polyvinyl chloride (PVC), and several other

polymers. PVC is used in wire insulation, pipes, and electronics. In addition, chlorine is very useful in the pharmaceutical industry. Medicinal products containing chlorine are used to treat infections, allergies, and diabetes. The neutralized form of hydrochloride is a component of many medications. Chlorine is also used to sterilize hospital machinery and limit infection growth. In agriculture, chlorine is a component of many commercial pesticides: DDT (dichlorodiphenyltrichloroethane) was used as an agricultural insecticide, but its use was discontinued.

**Bromine.** Bromine is used in flame retardants because of its fire-resistant properties. It is also found in the pesticide methyl bromide, which facilitates the storage of crops and eliminates the spread of bacteria. However, the excessive use of methyl bromide has been discontinued due to its impact on the ozone layer. Bromine is involved in gasoline production as well. Other uses of bromine include the production of photography film, the content in fire extinguishers, and drugs treating pneumonia and Alzheimer's disease.

**Iodine.** Iodine is important in the proper functioning of the thyroid gland of the body. If the body does not receive adequate iodine, a goiter (enlarged thyroid gland) will form. Table salt now contains iodine to help promote proper functioning of the thyroid hormones. Iodine is also used as an antiseptic. Solutions used to clean open wounds likely contain iodine, and it is commonly found in disinfectant sprays. In addition, silver iodide is important for photography development.

**Astatine.** Because astatine is radioactive and rare, there are no proven uses for this halogen element. However, there is speculation that this element could aid iodine in regulating the thyroid hormones. Also, it has been used in mice to aid the study of cancer.

### Halogen derivatives

Compounds derived from hydrocarbons by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are known as halogen derivatives. The halogen derivatives are classified on the basis of nature of hydrocarbon from which they are obtained as:

- alkyl halides (halogen derivatives of alkanes);
- alkenyl halides (halogen derivatives of alkenes);
- alkynyl halides (halogen derivatives of alkynes);
- aryl halides (halogen derivatives of arenes).

The *alkyl halides* (also known, as halogenoalkanes or haloalkanes) are a group of chemical compounds derived from alkanes containing

one or more halogens. They have the general formula  $RX$ , where  $R$  is an alkyl or substituted alkyl group and  $X$  is a halogen (F, Cl, Br, I). Haloalkanes are widely used commercially and, consequently, are known under many chemical and commercial names. They are used as flame retardants, fire extinguishants, refrigerants, propellants, solvents, and pharmaceuticals. Many halocarbons are serious pollutants and toxins. Haloalkanes which contain chlorine, bromine, and iodine are a threat to the ozone layer, but fluorinated volatile haloalkanes in theory may have activity as greenhouse gases.

While most haloalkanes are human-produced, non-artificial haloalkanes do occur on Earth, mostly through enzyme-mediated synthesis by bacteria, fungi, and especially sea macroalgae (seaweeds). More than 1600 halogenated organics have been identified, with bromoalkanes being the most common haloalkanes.

Haloalkanes generally resemble the parent alkanes in being colorless, relatively odorless, and hydrophobic. Their boiling points are higher than those of the corresponding alkanes. They are less flammable than alkanes, and some are used in fire extinguishers. Haloalkanes are better solvents than the corresponding alkanes because of their increased polarity. Haloalkanes containing halogens other than fluorine are more reactive than the parent alkanes.

The most readily available *alkenyl halide* is chloroethene (vinyl chloride). Chloroethene is produced in large quantities for the production of polymers. These polymers commonly are described as PVC plastics or less specifically as “vinyl”. They are materials that may be either flexible or rigid according to what they are mixed with, and they are used in the manufacture of many familiar articles such as plastic curtains, rainwear, floor tile, synthetic leather goods, upholstery, table mats, insulation, plastic pipes, tubing and packaging materials.

*Alkynyl halides* belong to one of the most useful and well-investigated classes of substituted alkynes. By analogy with alkyl and alkenyl halides these compounds can be expected to be valuable precursors in the synthesis of various alkynes by acetylenic nucleophilic substitution. Alkynyl halides can be effective building blocks in organic synthesis.

The stability and physical and chemical properties of alkynyl halides vary in a broad range depending on the nature of the halogen. Alkynyl fluorides are the least stable and the chemistry of these compounds is quite different from that of other alkynyl halides. The first

synthesis of alkynyl fluorides was only reported in 1959. Only a few examples of alkynyl fluorides are known, namely fluoroethyne, difluoroethyne, fluorochloroethyne, perfluoropropyne, t-butyl fluoroethyne, and fluoropropioly fluoride. All of these compounds are highly unstable and require special caution in their preparation and handling.

*Alkynyl chlorides, bromides and iodides* are relatively stable and have been known since the 19<sup>th</sup> century. A large variety of alkynyl chlorides are known. The first preparation of the parent representative of the class, monochloroethyne, was reported in 1880 by the pyrolysis of dichloroacrylic acid. A number of more convenient synthetic procedures based on dehydrochlorination of polychlorinated ethenes with different bases have been developed more recently.

*Alkynyl iodides* are best prepared by the direct iodination of terminal alkynes or the corresponding alkynylides. Iodine in liquid ammonia has been found to be very effective for the direct iodination of free alkynes.

The newest member of the family of alkynyl halides, alkynyliodonium salts, only became readily available in the 1980. In the decade 1993–2003, there has been a substantial interest in the synthetic application of alkynyl halides (mainly bromides, iodides and alkynyliodonium salts), which are valuable precursors in the synthesis of various alkynes reactions.

In organic chemistry, an *aryl halide* (also known as haloarene or halogenoarene) is a compound in which the halogen is attached directly to an aromatic ring. Carbon-halogen bonds in aryl halides are shorter and stronger than carbon-halogen bonds in alkyl halides. Because the carbon-halogen bond is stronger, aryl halides react more slowly than alkyl halides when carbon-halogen bond breaking is rate determining.

Aryl halides are colourless oily liquids having characteristic odour of aromatic compounds. In spite of the fact that aryl halides are polar molecules they are insoluble in water. This is because aryl halides cannot form hydrogen bond with water. However aryl halides are soluble in organic solvents like alcohol, ether etc. The aryl halides in general are heavier than water.

Aryl halides occur widely in nature, most commonly produced by marine organisms that utilize the chloride and bromide in ocean waters. Chlorinated and brominated aromatic compounds are also numerous, e. g. derivatives of tyrosine, tryptophan, and various pyrrole derivatives. Some of these naturally occurring aryl halides exhibit useful medicinal properties.

Aryl halides react with metals to give more reactive derivatives that behave as sources of aryl anions. Magnesium aryl halides are Grignard reagents, which are useful in organic synthesis of other aryl compounds. At high temperatures, aryl groups react with ammonia to give anilines.

Aryl halides most often are synthetic intermediates for the production of other useful substances.

### ◆ REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. In what physical states do halogens occur? 2. Why are halogens never found in nature in their native form? 3. What are the elements of the halogen family? 4. Where are organic compounds containing halogens used? 5. How are halogen derivatives classified? 6. Why are aryl halides insoluble in water? 7. What do physical and chemical properties of alkynyl halides depend on?

#### Ex. 2. Match the words with their definitions.

- |                      |   |
|----------------------|---|
| 1) halogens          | a) the lightest halogen which exists as a highly toxic, pale yellow diatomic gas                            |
| 2) nonmetal          | b) a compound added to manufactured materials that inhibit, suppress or delay the production of flame       |
| 3) electronegativity | c) a chemical element that mostly lacks metallic attributes   |
| 4) fluorine          | d) a group in the periodic table consisting of five chemically related elements (chlorine, bromine, etc.)   |
| 5) propellant        | e) a binary compound of which one part is a halogen atom and the other part is an element or radical        |
| 6) flame retardant   | f) a pressurized gas that is used to create movement of a fluid   |
| 7) halide            | g) a measure of the ability of an atom of one element to remove an electron from an atom of another element |

#### Ex. 3. Say whether the following statements are true or false.

1. Iodine is the most reactive halogen. 2. The halogens are poor thermal and electrical conductors in all phases. 3. Halogens require one additional electron to form a full octet. 4. Elemental halogens are di-

atomic molecules with non-polar covalent triple bonds. 5. Fluorine is the least electronegative element in the Periodic Table. 6. Astatine is widely distributed in nature. 7. Compounds containing more than one kind of halogen are possible.

**Ex. 4. Insert the necessary word.**

1. Halogens have relatively low melting and boiling points that ... steadily down the group. 2. The halogens have distinctive, unpleasant ..., and are toxic. 3. Halogens are so ... that all the elements except helium and neon react with at least one of the halogens. 4. Bromine consists of bromide ... which have been found in the sea. 5. The ... of iodine may increase if particular iodides are mixed in the solution. 6. Medicinal products containing ... are used to treat infections, allergies, and diabetes. 7. ... which contain chlorine, bromine, and iodine are a threat to the ozone layer.

solubility, odours, chlorine, salts, haloalkanes, increase, reactive

# UNIT VIII

## NITRO COMPOUNDS

A wide variety of organic compounds contain nitrogen. In fact, the types of nitrogen compounds are so numerous and diverse that we shall be unable to consider them all.

Nitro compound is any of a family of chemical compounds in which the nitro group ( $-\text{O}-\text{N}=\text{O}$ ) forms part of the molecular structure. The most common examples are organic substances in which a carbon atom is linked by a covalent bond to the nitrogen atom of the nitro group. The structure of a nitro group can be represented as a resonance hybrid of two equivalent zwitter ionic polar structures. The hybrid structure has a positively charged nitrogen and two equivalent negatively charged oxygens.

### Physical properties of nitro compounds

Nitro compounds have large dipole moments compared to other simple organic compounds. Due to the polarity, their boiling points are unusually high in comparison with other compounds of same molecular mass.

Lower nitro alkanes are colorless liquids with a pleasant smell. Higher members are solids. Aromatic nitro compounds like nitro benzene has a smell of bitter almonds.

Nitro alkanes are sparingly soluble in water (lower members are relatively more soluble than the higher members). Aromatic nitro compounds are not soluble in water. They are soluble in organic solvents.

The formal positive charge on nitrogen of nitro group makes it a strong electron withdrawing group and exerts a strong pull on neighboring electrons. The presence of nitro group in phenols enhances their acidity. In aromatic compounds, the nitro group deactivates then towards electrophilic substitution.

The nitro group is an ambident group and is capable of being attached to carbon chain through nitrogen as well as through oxygen atom.

Nitro compounds are named by using the prefix nitro before the name of parent hydrocarbon. The position of nitro group and other substituents are indicated by Arabic numerals:

$\text{CH}_3-\text{NO}_2$  – nitromethane;  $\text{CH}_3-\text{CH}_2-\text{NO}_2$  – nitroethane.

Aliphatic nitro compounds are called nitroalkanes while aromatic nitro compounds are called nitroarenes. The compound in which the  $-\text{NO}_2$  group is linked to the alkyl or aryl group through oxygen atom are

called nitrites. Nitrites are isomeric with nitro compounds. Amines and amides represent the two largest classes of nitrogen compounds.

Many nitro compounds are commercially produced for use as explosives, solvents, or chemical intermediates (substances valued as raw materials in further chemical processing).

### Amines

Amines are organic compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are derivatives of ammonia. Amine bases are classified according to the number of alkyl or aryl groups attached to nitrogen. Nitro compounds may be aliphatic or aromatic compounds according to whether the nitro group is attached to alkyl or aryl groups:

R – NO<sub>2</sub> – aliphatic nitro compounds;

Ar – NO<sub>2</sub> – aromatic nitro compound.

The aliphatic nitro compounds may be further classified into primary, secondary, tertiary nitro compounds according as the nitro group is attached to primary, secondary or tertiary carbon atom respectively.

A large and widespread class of naturally occurring amines is known as alkaloids. These are basic organic nitrogen compounds, mostly of plant origin. The structures of the plant alkaloids are extraordinarily complex, yet they are related to the simple amines in being weak nitrogen bases. In fact, the first investigator to isolate an alkaloid in pure form was F. W. A. Sertirner who, in 1816, described morphine as basic, salt-forming, and ammonialike. He used the term “organic alkali” from which is derived the name alkaloid.

Many of the alkaloids are of polycyclic structures and have other functional groups in addition to basic nitrogen. The nitrogens of alkaloids frequently have tertiary amine functions.

All of the alkaloids are substances with very pronounced physiological action. Indeed, alkaloids in general have been used and abused for centuries as medicinals, drugs, and poisons. However, their structures have become known only in this century, and we are still a long way from understanding the chemistry that leads to their pronounced physiological effects.

Alkaloids include compounds that may be classified as antimicrobial (quinine), as analgesics (morphine, codeine), as hallucinogens (mescaline, LSD), as stimulants (cocaine, atropine, caffeine) and as topical anaesthetics (cocaine). Although some of these compounds are

used as natural medicines, an entire industry has developed in an effort to produce synthetic analogs with similar, but safer, medicinal properties. Some of the better known of these synthetic drugs include a group of narcotic substances known as barbiturates, which are used widely as sedatives, anticonvulsants, tranquilizing drugs, synthetic stimulants, and antibiotics.

Basic nitrogen compounds similar to the plant alkaloids also occur in animals, although the description animal alkaloid seldom is used. Certain amines and ammonium compounds play key roles in the function of the central nervous system and the balance of amines in the brain is critical for normal brain functioning. Also, many essential vitamins and hormones are basic nitrogen compounds. Nitrogen bases also are vital constituents of nucleic acid polymers (DNA and RNA) and of proteins.

Everyone who works with organic chemicals should be aware that a number of arenamines are carcinogens. The most dangerous examples are known to induce human bladder cancer. These chemicals were used widely in the chemical industry (mostly in azo dye manufacture) long before they were recognized as hazardous carcinogens. Voluntary action and appropriate legislation now controls the industrial uses of these substances, and there also are some controls for uses in research and teaching. It is important to be aware of the potential hazards of known carcinogens and to recognize that all chemicals, both organic and inorganic, should be treated with great respect if their thermodynamic and physiological properties are not known. Carcinogenic character is just one of many possible hazards.

There is an unresolved problem related to the carcinogenic properties of nitroso compounds. You probably are aware (if you read the labels on food packages) that sodium nitrite is added to many packaged meat products. Sodium nitrite prevents the growth of harmful bacteria, thereby retarding spoilage, and it also enhances the appearance by maintaining the red look of fresh meat. There is a possibility that nitrite may have adverse effects on human health by nitrosating the amino and amide functions of proteins in the presence of acids. This possibility has to be balanced against the alternate threat to human health if the use of nitrite were discontinued, that of increased food spoilage. In any case, it seems clear that the amount of sodium nitrite actually used in most processing is in excess of that needed to retard bacterial decay.

## The physical properties of amines

The physical properties of amines depend in an important way on the extent of substitution at nitrogen. Thus primary amines,  $\text{RNH}_2$ , and secondary amines,  $\text{R}_2\text{NH}$ , are less volatile than hydrocarbons of similar size, weight, and shape. The physical properties of tertiary amines are similar to those of hydrocarbons of similar branching and molecular weights.

The water solubilities of the lower-molecular-weight amines are appreciable. Amines are more water-soluble than alcohols of similar molecular weights.

Amines, especially those with significant volatility, have unpleasant odors. Some of them smell like ammonia, others smell fishy, while others are indescribably revolting.

Perhaps the most characteristic property of amines is their ability to act as bases by accepting protons from a variety of acids. Primary and secondary amines are very weak acids.

## Amides

The properties of the simple amides are relevant to the chemistry of peptides and proteins, substances that are fundamental to all life as we know it. Indeed, the characteristics of peptides and proteins are primarily due to their polyamide structures. For this reason, it is important to know and understand the chemistry of simple amides.

The simple amides are named either as *alkanamides*, in which the prefix alkan(e) is determined by the longest carbon chain that includes the carbonyl group (methanamide), or as substituted *carboxamides*, in which the name is completed by identifying the R substituent.

The degree of substitution on the amide nitrogen determines whether the amide is primary  $\text{RCONH}_2$ , secondary  $\text{RCONHR}$ , or tertiary  $\text{RCONR}_2$ .

When the amide is secondary or tertiary, the symbol N (for nitrogen) must precede the name of each different group attached to nitrogen.

Amides still are very weak acids (about as weak as water) and, for practical purposes, are regarded as neutral compounds. The degree of basicity of amides is very much less than that of aliphatic amines.

## Various methods of organic synthesis of nitro compounds

There are seemingly many different ways in which amines can be prepared.

A nitro compound ordinarily is made by the reaction, called *nitration*, between nitric acid and an organic compound. Nitration of aromatic compounds, such as benzene or toluene, is commonly effected by treating them with a mixture of nitric and sulfuric acids at temperatures of 100°C or lower. These temperatures are not high enough for nitrating aliphatic compounds; propane, however, is commercially converted to a mixture of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane by allowing it to react with nitric acid vapours at temperatures of about 400°C. The mixture is then separated into its components by fractional *distillation*.

The most important reaction of aromatic nitro compounds is their *reduction*, which can be brought about by a wide variety of agents. Under acidic conditions, reduction almost always produces an amine. In neutral media, reduction may yield a hydroxylamine. In alkaline solution, compounds containing nitrogen-to-nitrogen bonds (azo, hydrazo, or azoxy compounds) are formed.

*Hydrolysis* of aliphatic nitro compounds is also widely used. Primary aliphatic nitro compounds can be converted to aldehydes by treatment of their carbanion salts with sulphuric acid. When primary nitro compounds are treated with H<sub>2</sub>SO<sub>4</sub> without prior conversion to salts, they give carboxylic acids. Secondary nitro alkanes hydrolyze with boiling HCl to give ketones and nitrous oxide.

Amino groups are particularly susceptible to reactions with a wide variety of reagents, especially oxidizing reagents, alkylating reagents, and many carbonyl compounds. Therefore, if we wish to prevent the amino group from undergoing undesired reactions while chemical change occurs elsewhere in the molecule, it must be suitably protected (protonation, alkylation, acylation, sulfonylation).

Amides generally are formed from acid chlorides, acid azides, acid anhydrides, and esters. It is not practical to prepare them directly from an amine and a carboxylic acid without strong heating or unless the reaction is coupled to a second reaction that “activates” the acid.

The hydrolysis of nitriles is a satisfactory method for preparation of unsubstituted amides and is particularly convenient when hydrolysis is induced under mildly basic conditions by hydrogen peroxide.

A nitrile is any organic compound that has a  $-C\equiv N$  functional group. The prefix *cyano-* is used interchangeably with the term nitrile in industrial literature. Nitriles are found in many useful compounds, including methyl cyanoacrylate, used in super glue, and nitrile rubber,

a nitrile-containing polymer used in the latex-free laboratory and medical gloves. Nitrile rubber is also widely used as automotive and other seals since it is resistant to fuels and oils. Organic compounds containing multiple nitrile groups are known as cyanocarbons.

## ◆ REVISION EXERCISES

### Ex. 1. Answer the following questions.

1. What is a nitro compound? 2. What are physical properties of nitro compounds? 3. What is indicated by Arabic number? 4. Why are nitro compounds commercially produced? 5. What are amines? 6. What is the difference between aliphatic or aromatic compounds? 7. What are physical properties of amines? 8. What are amides? 9. Which methods of organic synthesis of nitro compounds are the most widely used? 10. What is a nitrile?

### Ex. 2. Match the words with their definitions.

- |                            |   |
|----------------------------|---|
| 1) alkaloid                | a) a substance that can cause cancer  |
| 2) antibiotic              | b) the opposite of oxidation  |
| 3) derivative              | c) something that involves the sharing of electron pairs between atoms                        |
| 4) carcinogen              | d) a drug that is used to kill bacteria and cure infections                                   |
| 5) covalent bond           | e) to improve something   |
| 6) fractional distillation | f) a group of naturally occurring chemical compounds that contain mostly basic nitrogen atoms |
| 7) enhance                 | g) something that has developed or been produced from something else                          |
| 8) reduction               | h) the separation of a mixture into its component parts                                       |

### Ex. 3. Say whether the following statements are true or false.

1. The types of nitrogen compounds are so rare and unique that know all of them by heart. 2. The boiling points of nitro compounds differ from those of other compounds of same molecular mass. 3. All nitro compounds are readily soluble in water. 4. Nitro compounds are widely used in industry. 5. Alkaloids are basic organic amines mostly of plant origin. 6. Essential vitamins and hormones don't contain any nitrogen in its composition. 7. Amines normally have very pleasant

smell of bitter almonds. 8. Everybody who studies peptides and proteins should know a lot about the chemistry of simple amides. 9. Hydrolysis of aliphatic nitro compounds is the most expensive and unpopular way of organic synthesis of nitro compounds.

**Ex. 4. Insert the necessary word.**

1. Nitroglycerine ... first by Ascanio Sobrero, an Italian chemist at the University of Turin. 2. Like nitrocellulose, nitroglycerine can be thought of as a glycerol-... with nitro-groups. 3. The addition of sulfuric acid and nitric acid to glycerol leads to the O-nitration of glycerol, whereby the nitro-group ... the protons of glycerol's hydroxyl groups. 4. However, unlike nitrocellulose nitroglycerin's molecular make up ... it to exothermically decompose into gases without an external oxygen source; rather than deflagrating, nitroglycerin detonates. 5. Unfortunately, the ... of nitroglycerine has a very low activation energy barrier; which makes nitroglycerine susceptible to explosion upon physical contact, and thus impractical for use in most contexts. 6. By 1867, however, Alfred Nobel was able to calm the shock sensitivity of nitroglycerin ... .

was synthesized, allows, derivative, replaces, to produce dynamite, combustion
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# UNIT IX

## ALCOHOLS

The products of replacement of hydrogen in hydrocarbons by the hydroxyl group (hydroxyl group) are known as alcohols. The general formula for an alcohol is ROH, the R representing the aliphatic portion of the molecule, alcohols may be regarded as derivatives of water in which an alkyl group replaces one hydrogen atom. The alcohols bear some physical resemblance both to the hydrocarbons and water. The best known member of the class is ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ . It is soluble both in water and in gasoline. Its boiling point is lower than that of water, although its molecular weight is much greater.

The hydroxyl derivatives of aromatic hydrocarbons are called aromatic alcohols when the hydroxyl group is in the side chain and phenols when the hydroxyl group is attached directly to a benzene ring.

Aliphatic alcohols are divided into saturated and unsaturated ones in conformity with the nature of the hydrocarbon radical.

The characteristic functional group of alcohols is hydroxyl or  $-\text{OH}$  group. Depending on the number of  $-\text{OH}$  groups in the molecule the alcohols are classified into monohydric, dihydric, trihydric, and polyhydric alcohols.

The isomerism of alcohols is caused by the structure of the radical (isomerism of the carbon skeleton) and the position of the hydroxyl (position isomerism). There are primary I, secondary II, and tertiary III alcohols in conformity with the position of the hydroxyl in the molecule, depending on the carbon (primary, secondary, or tertiary one) with which it is linked.

There are several general methods of alcohol preparation:

1. The hydration of olefins in the acid medium. This method is of great importance, because it allows us to obtain alcohols from gases of petroleum cracking. Primary alcohol, or ethanol, is obtained from ethylene, while only secondary and tertiary alcohols are obtained from other olefins. The method of direct hydration is used industrially; it is carried out by passing a mixture of olefin and water vapour over a phosphate catalyst.

2. Another important industrial method is the fermentation of carbohydrates.

3. Hydrolysis of the halogen derivatives. This method is important in obtaining alcohols from hydrocarbons.

## Physical properties of alcohols

The lower and middle members of the series of saturated monohydric alcohols ( $C_1$ – $C_{11}$ ) are liquids whose boiling points rise as the composition becomes more complex. Higher alcohols from  $C_{12}$  are solids. Alcohols having an iso-structure boil at a lower temperature than those having a normal structure. The lower representatives have a characteristic alcoholic odour and a burning taste, the middle representatives  $C_4$ – $C_6$  have an unpleasant odour, and the higher ones are odourless. The density of alcohols is less than unity, and only that of some of aromatic alcohols is higher than unity. The first three members of the saturated alcohols mix with water in all proportions, but solubility diminishes as the radical becomes more complex. Higher alcohols, like hydrocarbons are practically water insoluble.

The molecules of alcohols in solid and liquid state, like water molecules, are associated; in this case, the molecular mass of a substance considerably increases and consequently, its volatility decreases. Association is interrupted as alcohols pass over to a vapour state. Association is caused by hydrogen bonds which originate between molecules.

## Chemical properties of alcohols

The functional group of alcohols, the hydroxyl, determines the main chemical properties of these compounds. Alcohols are characterized by great chemical activity.

**Acid and basic properties.** Formation of alkoxides. Alcohols are practically neutral substances: they do not change the colour of indicators and do not react with either aqueous solutions of alkalis or dilute acids. However, in certain reactions, alcohols exhibit properties of a very weak acids and bases, i. e. they are amphoteric, like water. When alkali metals act on alcohols in anhydrous medium, hydroxyl hydrogen is forced out and alkoxides are formed. Alkoxides have the nature of salts of a very weak acid with a base. The basic properties of alcohols are exhibited in their interaction with strong acids. In this case, alcohols like water yield oxonium salts.

**Formation of ethers.** Ethers are obtained when alkoxides react with alkyl halides.

**Dehydration of alcohols.** Alcohols are capable of losing water under definite conditions. Concentrated sulphuric or phosphoric acid can be used as dehydrating agent. Alcohols dehydrate when their vapours are passed over a heated solid catalyst (silica gel, aluminium oxide, etc.).

**Oxidation of alcohols.** Different products can be formed, depending on the nature of alcohols and reaction conditions. Primary alcohols yield at first aldehydes, and then acids having the same number of carbon atoms. Ketones are formed from secondary alcohols. Tertiary alcohols are more stable towards oxidation.

**Catalytic dehydrogenation of alcohols.** Alcohols can be converted into aldehydes and ketones also by dehydrogenation, i. e. by passing alcohol vapours over a heated metallic catalyst such as copper or silver at 300°C. A typical dehydrogenation reaction is the conversion of ethyl alcohol into acetaldehyde. This reaction is endothermic.

### Preparation of alcohols

**Functional group transformation.** Alcohols can be prepared by nucleophilic substitution of alkyl halides, hydrolysis of esters, reduction of carboxylic acids or esters, reduction of aldehydes or ketones, electrophilic addition of alkenes, hydroboration of alkenes, or substitution of ethers.

**C–C bond formation.** Alcohols can also be obtained from epoxides, aldehydes, ketones, esters, and acid chloride as a consequence of C–C bond formation. These reactions involve the addition of carbanion equivalents through the use of Grignard or organolithium reagents.

### REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. What are alcohols?
2. What is the general formula of alcohols?
3. What groups are alcohols classified into?
4. What does isomerism of alcohols determine?
5. What are the methods of alcohol preparation?
6. What are the physical properties of alcohols?

#### Ex. 2. Match the words with their definitions.

- |               |   |
|---------------|---|
| 1) volatility | a) the quantity per unit volume, unit area, or unit length as the mass of a substance per unit volume   |
| 2) derivative | b) the state of looking or being like someone or something else, correspondence in appearance or superficial qualities, a point of likeness, similarity |
| 3) density    | c) something that comes from something else, substance that is made from another substance  |

- 4) resemblance      d) the property of certain substances in very small concentrations to stimulate chemical sense receptors that sample the air or water surrounding the animal
- 5) odour              e) a substance that has a bitter taste and that forms a salt when mixed with an acid; a soluble salt obtained from the ashes of plants and consisting largely of potassium or sodium carbonate; a substance (as a hydroxide or carbonate of alkali metal) having marked basic properties
- 6) alkali              f) state of being readily vaporizable at a relatively low temperature

**Ex. 3. Say whether the following statements are true or false.**

1. Alcohols dehydrate when their vapours are passed over a heated solid catalyst. 2. The prefix *cyclo-* is used for alcohols with straight-chain alkyl groups. 3. Alcohols can be converted into aldehydes and ketones also by hydration. 4. The first three members of the saturated alcohols mix with water in all proportions. 5. The isomerism of alcohols is caused by the structure of the chain. 6. The lower alcohol representatives have a characteristic alcoholic odour and a burning taste.

**Ex. 4. Insert the necessary word.**

1. Alcohols are among the most common organic compounds. 2. They are used as ... and in making perfumes, are valuable intermediates in the synthesis of other compounds, and are among the most abundantly produced organic ... in industry. 3. Perhaps the two best-known alcohols are ... and methanol (or methyl alcohol). 4. Ethanol is used in toiletries, pharmaceuticals, and fuels, and it is used to ... hospital instruments. 5. It is, moreover, the alcohol ... . 6. The anesthetic ether is also made from ... . 7. Methanol is used as solvent, as raw material for the manufacture of formaldehyde and special resins, in special fuels, in antifreeze, and for cleaning metals. 8. Alcohols may be classified as primary, secondary, or tertiary, according to which carbon of the alkyl group is bonded to the ... group. 9. Most alcohols are colourless liquids ... at room temperature. 10. Alcohols of low molecular weight are highly ... in water; with increasing molecular weight, they become less soluble in water, and their boiling points, vapour pressures, densities, and viscosities increase.

solids, beverages, chemicals, ethanol ( $\times 2$ ), sweeteners, soluble, hydroxyl, sterilize

**Ex. 5. Translate the following text.****Nomenclature**

As with other types of organic compounds, alcohols are named by both formal and common systems. The most generally applicable system is that adopted at a meeting of the International Union of Pure and Applied Chemistry (IUPAC) in Paris in 1957. Using the IUPAC system, the name for an alcohol uses the *-ol* suffix with the name of the parent alkane, together with a number to give the location of the hydroxyl group. The rules are summarized in a three-step procedure:

*Name* the longest carbon chain that contains the carbon atom bearing the  $\text{-OH}$  group.

*Drop* the final *-e* from the alkane name, and add the suffix *-ol*.

*Number* the longest carbon chain starting at the end nearest the  $\text{-OH}$  group, and use the appropriate number, if necessary, to indicate the position of the  $\text{-OH}$  group.

*Name* the substituents, and give their numbers as for an alkane or alkene.

The first example below has a longest chain of six carbon atoms, so the root name is hexanol. The  $\text{-OH}$  group is on the third carbon atom, which is indicated by the name 3-hexanol. There is a methyl group on carbon 3 and a chlorine atom on carbon 2. The complete IUPAC name is 2-chloro-3-methyl-3-hexanol. The prefix *cyclo-* is used for alcohols with cyclic alkyl groups. The hydroxyl group is assumed to be on carbon 1, and the ring is numbered in the direction to give the lowest possible numbers to the other substituents, as in, for example, 2,2-dimethylcyclopentanol.

**Common names.** The common name of an alcohol combines the name of the alkyl group with the word alcohol. If the alkyl group is complex, the common name becomes awkward and the IUPAC name should be used. Common names often incorporate obsolete terms in the naming of the alkyl group; for example, amyl is frequently used instead of pentyl for a five-carbon chain.

# UNIT X

## PHENOLS

Phenol like any of a family of organic compounds is characterized by a hydroxyl ( $\text{-OH}$ ) group attached to a carbon atom that is part of an aromatic ring. Besides serving as the generic name for the entire family, the term phenol is also the specific name for its simplest member, monohydroxybenzene ( $\text{C}_6\text{H}_5\text{OH}$ ), also known as benzenol, or carboic acid.

**Physical properties of phenols.** Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic. Similar to alcohols, phenols have hydroxyl groups that can participate in intermolecular hydrogen bonding; in fact, phenols tend to form stronger hydrogen bonds than alcohols. Hydrogen bonding results in higher melting points and much higher boiling points for phenols than for hydrocarbons with similar molecular weights. For example, phenol (molecular weight [MW] 94, boiling point [b. p.]  $182^\circ\text{C}$  [ $359.6^\circ\text{F}$ ]) has a boiling point more than 70 degrees higher than that of toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ ; MW 92, b. p.  $111^\circ\text{C}$  [ $231.8^\circ\text{F}$ ]).

Phenols are widely used in household products and as intermediates for industrial synthesis. For example, phenol itself is used (in low concentrations) as a disinfectant in household cleaners and in mouthwash. Phenol may have been the first surgical antiseptic. In 1865 the British surgeon Joseph Lister used phenol as an antiseptic to sterilize his operating field. With phenol used in this manner, the mortality rate from surgical amputations fell from 45 to 15 percent in Lister's ward. Phenol is quite toxic, however, and concentrated solutions cause severe but painless burns of the skin and mucous membranes. Less-toxic phenols, such as *n*-hexylresorcinol, have supplanted phenol itself in cough drops and other antiseptic applications. Butylated hydroxytoluene (BHT) has a much lower toxicity and is a common antioxidant in foods.

In industry, phenol is used as a starting material to make plastics, explosives such as picric acid, and drugs such as aspirin. Substituted phenols are used in the dye industry to make intensely coloured azo dyes. Mixtures of phenols (especially the cresols) are used as components in wood preservatives such as cresote. Phenol, the cresols (methylphenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum.

## Natural sources of phenols

Phenols are common in nature; examples include tyrosine, one of the standard amino acids found in most proteins; epinephrine (adrenaline), a stimulant hormone produced by the adrenal medulla; serotonin, a neurotransmitter in the brain; and urushiol, an irritant secreted by poison ivy to prevent animals from eating its leaves. Many of the more complex phenols used as flavourings and aromas are obtained from essential oils of plants. For example, vanillin, the principal flavouring in vanilla, is isolated from vanilla beans, and methyl salicylate, which has a characteristic minty taste and odour, is isolated from wintergreen. Other phenols obtained from plants include thymol, isolated from thyme, and eugenol, isolated from cloves.

### REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. What is the definition of phenols? 2. What is the common feature between phenols and alcohols? 3. What are the physical properties of phenols? 4. Where are phenols used in industry and household utilities production? 5. What are the natural sources of phenols?

#### Ex. 2. Match the words with their definitions.

- |                   |  |
|-------------------|--|
| 1) caustic        | a) any of a large class of volatile odoriferous oils of vegetable origin that give plants their characteristic odours and often other properties from different parts of plants (flowers, leaves, or bark) by steam distillation, expression, or extraction that are usually mixtures of compounds, and that are often used in the form of essences in perfumes, flavorings, and pharmaceutical preparations |
| 2) dye            | b) to stop from happening and existing   |
| 3) generic        | c) joined together, especially in pairs; acting or operating as if joined  |
| 4) essential oils | d) able to destroy or burn something by chemical action  |
| 5) prevent        | e) related or having the rank of a biological genus  |
| 6) conjugate      | f) a soluble or insoluble coloring material  |

#### Ex. 3. Say whether the following statements are true or false.

1. The ability of phenols to form strong hydrogen bonds also enhances their solubility in water. 2. Many of the more complex phenols

used as flavourings. 3. Like other alcohols, phenols undergo dehydration. 4. Benzene is derived from chlorobenzene by a variety of methods. 5. Phenols are rarely used in household products and as intermediates for industrial synthesis. 6. Phenols occur either as colourless liquids or white solids at room temperature.

**Ex. 4. Insert the necessary word.**

1. Phenols are compounds that have an OH group directly attached to an aromatic ring. 2. Therefore, the oxygen is  $sp^3$  hybridised and the aryl carbon is  $sp^2$  ... . 3. Although phenols share some characteristics with alcohols, they have distinct properties and reactions that set them apart from that functional group. 4. Phenols can participate in intermolecular hydrogen ... that means that they have moderate water ... and have higher boiling points than aromatic compounds lacking the phenolic group. 5. Phenols are weakly ..., and in aqueous solution an equilibrium exists between the phenol and the phenoxide ion. 6. When treated with a base, the phenol gets converted to the phenoxide ion. The phenoxide ion is stabilised by resonance and delocalisation of the negative charge into the ring, therefore phenoxide ions are weaker bases than alkoxide ions. 7. This means that phenols are more acidic than alcohols, but less acidic than carboxylic acids. 8. They are useful reagents in organic synthesis. 9. The ability of phenols to form strong hydrogen bonds also enhances their ... in water. 10. Phenol ... to give a 9.3 percent solution in water, compared with a 3.6 percent solution for cyclohexanol in water. 11. The association between water and phenol is unusually strong; when crystalline phenol is left out in a humid environment, it picks up enough water from the air to form liquid droplets. 12. Synthesis of phenols: most of the phenol used today is produced from benzene, through either hydrolysis of chlorobenzene or oxidation of isopropylbenzene (cumene). 13. Hydrolysis of chlorobenzene (the Dow process): benzene is easily converted to chlorobenzene by a variety of methods, one of which is the Dow process. 14. Chlorobenzene is hydrolyzed by a strong base at high ... to give a phenoxide salt, which is acidified to phenol. 15. Oxidation of isopropylbenzene: benzene is converted to isopropylbenzene (cumene) by ... with propylene and an acidic catalyst. 16. ... yields a cumene hydroperoxide which undergoes acid-catalyzed rearrangement to phenol and acetone. 17. Although this process seems more complicated than the Dow process, it is advantageous because it produces two ... industrial products: phenol and acetone.

valuable, hybridized, temperatures, solubility ( $\times 2$ ), acidic, dissolves, charge, bonding, treatment, oxidation
---

**Ex. 5. Read the text and summarize the chemical properties of phenols.**

### Nomenclature of phenols

**General synthesis of phenols.** To make more complicated phenolic compounds, a more general synthesis is needed. The cumene hydroperoxide reaction is fairly specific to phenol itself. The Dow process is somewhat more general, but the stringent conditions required often lead to low yields, and they may destroy any other functional groups on the molecule. A milder, more general reaction is the diazotization of an arylamine (a derivative of aniline,  $C_6H_5NH_2$ ) to give a diazonium salt, which hydrolyzes to a phenol. Most functional groups can survive this technique, as long as they are stable in the presence of dilute acid.

**Reactions of phenols.** Much of the chemistry of phenols is like that of alcohols. For example, phenols react with acids to give esters, and phenoxide ions ( $ArO^-$ ) can be good nucleophiles in Williamson ether synthesis.

**Acidity of phenols.** Although phenols are often considered simply as aromatic alcohols, they do have somewhat different properties. The most obvious difference is the enhanced acidity of phenols. Phenols are not as acidic as carboxylic acids, but they are much more acidic than aliphatic alcohols, and they are more acidic than water. Unlike simple alcohols, most phenols are completely deprotonated by sodium hydroxide ( $NaOH$ ).

**Oxidation.** Like other alcohols, phenols undergo oxidation, but they give different types of products from those seen with aliphatic alcohols. For example, chromic acid oxidizes most phenols to conjugated 1,4-diketones called quinones. In the presence of oxygen in the air, many phenols slowly oxidize to give dark mixtures containing quinones.

**Hydroquinone.** 1,4-benzenediol is a particularly easy compound to oxidize, because it has two hydroxyl groups in the proper relationship to give up hydrogen atoms to form a quinone. Hydroquinone is used in developing photographic film by reducing activated (exposed to light) silver bromide ( $AgBr$ ) to black metallic silver ( $Ag\downarrow$ ). Unexposed grains of silver bromide react more slowly than the exposed grains.

# UNIT XI

## ETHERS

Ethers are a class of organic compounds that contains an oxygen atom connected to two alkyl or aryl groups. These groups are represented by letter "R". The general formula of ethers is R–O–R'. They can be classified into two varieties. If the alkyl groups are the same on both sides of the oxygen atom then it is a simple or symmetrical ether, e. g. diethyl ether, dimethyl ether etc. Whereas if they are different the ethers are called mixed or unsymmetrical ethers, e. g. methyl ethyl ether, methyl phenyl ether, etc. There are many specific types of ethers depending on what the "R" group is. They may be further classified as open-chain, cyclic, saturated, unsaturated, aromatic and so on.

One of the most common ethers is diethyl ether. Diethyl ether was one of the first anesthetics used in hospitals. Ethers are generally colourless, sweet-smelling liquids at room temperature. They have a low boiling point compared to water. Due to the structure of the molecule, ether is extremely flammable, which is partially why it is no longer used in medicine today.

The simple ethers do not have O–H bonds, and most of their reactions are limited to the substituent groups. The chemistry of ethers, therefore, is less varied than that of alcohols. This fact is turned to advantage in the widespread use of ethers as solvents for a variety of organic reactions.

Simple ethers such as methyl or ethyl ethers usually are not suitable protecting groups because they cannot be removed except under rather drastic conditions.

Unlike alcohols, ethers are not acidic and usually do not react with bases. However, exceptionally strong basic reagents, particularly certain alkali-metal alkyls, will react destructively with many ethers. Ethers can be cleaved under strongly acidic conditions by intermediate formation of dialkyloxonium salts. Hydrobromic and hydroiodic acids are especially useful for ether cleavage because both are strong acids and their anions are good nucleophiles. Tertiary alkyl ethers are very easily cleaved by acid reagents. Ethers are susceptible to attack by halogen atoms and radicals, and for this reason they are not good solvents for radical reactions. In fact, ethers are potentially hazardous chemicals, because in the presence of atmospheric oxygen radical-chain formation of peroxides occurs, and peroxides are unstable, explosion-

prone compounds. This process is called autoxidation and occurs not only with ethers but with many aldehydes and hydrocarbons.

In general, ethers are low on the scale of chemical reactivity because the carbon-oxygen bond is not cleaved readily. For this reason ethers frequently are employed as inert solvents in organic synthesis. Particularly important in this connection are diethyl ether, diisopropyl ether, tetrahydrofuran, and 1,4-dioxane.

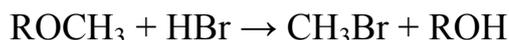
**Physical properties.** Ether molecules cannot form hydrogen bonds with each other, resulting in relatively low boiling points compared to those of the analogous alcohols. The difference, however, in the boiling points of ethers and their isomeric alcohols becomes lower as the carbon chains become longer, as the van der Waals interactions of the extended carbon chain dominates over the presence of hydrogen bonding.

Ethers are slightly polar. The C–O–C bond angle in the functional group is about  $110^\circ$ , and the C–O dipoles do not cancel out. Ethers are more polar than alkenes but not as polar as alcohols, esters, or amides of comparable structure. However, the presence of two lone pairs of electrons on the oxygen atoms makes hydrogen bonding with water molecules possible.

Ethers containing up to 3 carbon atoms are soluble in water due to their hydrogen bond formation with water molecules. The solubility decreases with an increase in the number of carbon atoms. The relative increase in the hydrocarbon portion of the molecule decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone, etc.

**Chemical reactions.** Ethers are quite stable chemical compounds which do not react with bases, active metals, dilute acids, oxidizing agents and reducing agents. Generally, they are of low chemical reactivity, but they are more reactive than alkanes. Important reactions are listed below.

**Acidic cleavage.** Although ethers resist hydrolysis, their polar bonds are cloven by mineral acids such as hydrobromic acid and hydroiodic acid. Hydrogen chloride cleaves ethers only slowly. Methyl ethers typically form methyl halides:



Some ethers undergo rapid cleavage with boron tribromide (even aluminium chloride is used in some cases) to give the alkyl bromide. Depending on the substituents, some ethers can be cloven with a variety of reagents, e. g. strong base.

**Peroxide formation.** When stored in the presence of air or oxygen, ethers tend to form explosive peroxides, such as diethyl ether peroxide. The reaction is accelerated by light, metal catalysts, and aldehydes. In conditions likely to form peroxides, it is recommended, when an ether is used as a solvent, not to distill it to dryness, as any peroxides that may have formed, being less volatile than the original ether, will become concentrated in the last few drops of liquid.

**Lewis bases.** Ethers serve as Lewis bases and Bronsted bases. Strong acids protonate the oxygen to give “onium ions” For instance, diethyl ether forms a complex with boron trifluoride, i. e. diethyl etherate. Ethers also coordinate to Mg (II) center in Grignard reagents. Polyethers, including many antibiotics cryptands, and crown ethers, bind alkali metal cations.

**Alpha-halogenation.** This reactivity is similar to the tendency of ethers with alpha hydrogen atoms to form peroxides. Reaction with chlorine produces alpha-chloroethers.

### Ether formation

Ethers can be prepared in the laboratory in several different ways.

**Dehydration of alcohols.** The dehydration of alcohols affords ethers at high temperature (about 125°C). The reaction is catalyzed by acids, usually sulfuric acid. The method is effective for generating symmetrical ethers, but not unsymmetrical ethers, since either OH can be protonated, which would give a mixture of products. Diethyl ether is produced from ethanol by this method. Cyclic ethers are readily generated in this way.

The dehydration route often requires conditions incompatible with delicate molecules.

The *Williamson ether synthesis* is an organic reaction, forming an ether from an organohalide and an alcohol. This reaction was developed by Alexander Williamson in 1850. Typically it involves the reaction of an alkoxide ion with a primary alkyl halide via an S<sub>N</sub>2 reaction.

The Williamson reaction is of broad scope, it is widely used in both laboratory and industrial synthesis, and remains the simplest and most popular method of preparing ethers. Both symmetrical and asymmetrical ethers are easily prepared. The intramolecular reaction of halohydrins in particular, gives epoxides.

In the case of asymmetrical ethers there are two possibilities for the choice of reactants, and one is usually preferable either on the basis

of availability or reactivity. The Williamson reaction is also frequently used to prepare an ether indirectly from two alcohols. One of the alcohols is first converted to a leaving group (usually tosylate), then the two are reacted together.

A typical Williamson reaction is conducted at 50–100°C and is complete in 1–8 hours. Often the complete disappearance of the starting material is difficult to achieve, and side reactions are common. Yields of 50–95% are generally achieved in laboratory syntheses, while near-quantitative conversion can be achieved in industrial procedures.

**Ullmann condensation.** The Ullmann condensation is similar to the Williamson method except that the substrate is an aryl halide. Such reactions generally require a catalyst, such as copper.

**Electrophilic addition of alcohols to alkenes.** Alcohols add to electrophilically activated alkenes. Acid catalysis is required for this reaction. Often, mercury trifluoroacetate ( $\text{Hg}(\text{OCOCF}_3)_2$ ) is used as a catalyst for the reaction generating an ether with Markovnikov regiochemistry. Using similar reactions, tetrahydropyranyl ethers are used as protective groups for alcohols.

### Ether usage

Ether is an organic compound that has sweet smell. Ether is colorless and evaporates very quickly when exposed to air. It catches fire very easily and needs to be handled with care. It is used as an antiseptic to prevent infection when an injection is administered. Cotton is dipped in ether and the skin is disinfected before an injection is allowed to pierce the skin.

At room temperature, ethers are pleasant-smelling colourless liquids. Relative to alcohols, ethers are generally less dense, less soluble in water, and have lower boiling points. They are relatively unreactive, and as a result they are useful as solvents for fats, oils, waxes, perfumes, resins, dyes, gums, and hydrocarbons. Vapours of certain ethers are used as insecticides, miticides, and fumigants for soil.

Ethers are also important in medicine and pharmacology, especially for use as anesthetics. For example, ethyl ether ( $\text{CH}_3\text{CH}_2\text{--O--CH}_2\text{CH}_3$ ), simply known as ether, was first used as a surgical anesthetic in 1842. Codeine, a potent pain-relieving drug, is the methyl ether of morphine. Because ether is highly flammable, it has largely been replaced by less-flammable anesthetics, including nitrous oxide ( $\text{N}_2\text{O}$ ) and halothane ( $\text{CF}_3\text{--CHClBr}$ ).

Ethyl ether is an excellent solvent for extractions and for a wide variety of chemical reactions. It is also used as a volatile starting fluid for diesel engines and gasoline engines in cold weather. Dimethyl ether is used as a spray propellant and refrigerant. Methyl *t*-butyl ether (MTBE) is a gasoline additive that boosts the octane number and reduces the amount of nitrogen-oxide pollutants in the exhaust. The ethers of ethylene glycol are used as solvents and plasticizers.

### ◆ REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. What are two varieties of ethers? 2. What are physical properties of ethers? 3. What catalysts are used for dehydration of ethers? 4. How long does a typical Williamson reaction proceed? 5. What are the most important ether reactions? 6. What is chemical reactivity of ethers? 7. Where are ethers used?

#### Ex. 2. Match the words with their definitions.

- |                |   |
|----------------|---|
| 1) anesthetics | a) the splitting of a complex molecule into simpler molecules; the breaking of a chemical bond in a molecule to give smaller molecules or radicals                            |
| 2) substituent | b) an atom, molecule, or ion that has unpaired valence electrons  |
| 3) solvent     | c) a chemical that is found in an air conditioner, a refrigerator, and in other equipment; a substance that undergoes phase transitions from a liquid to a gas and back again |
| 4) cleavage    | d) a drug that causes a reversible loss of sensation; a substance that is usually administered to facilitate surgery  |
| 5) anion       | e) an atom or a group of atoms that take the position of another atom in a molecule   |
| 6) radical     | f) a substance that dissolves a solute (a chemically different liquid, solid, or gas) resulting in a solution   |
| 7) refrigerant | g) an ion that has a negative charge, especially an ion that migrates to an anode in electrolysis   |

#### Ex. 3. Say whether the following statements are true or false.

1. Unlike alcohols ethers are not acidic and usually react with bases. 2. Ethers are susceptible to attack by halogen atoms and for this

reason they are good solvents for radical reactions. 3. Ether molecules cannot form hydrogen bonds with each other and this results in low boiling points compared to alcohols. 4. Ethers are quite stable chemical compounds which easily react with bases, active metals and dilute acids. 5. The main reactions of ethers are acidic cleavage, peroxide formation, alpha-halogenation. 6. The Williamson ether synthesis is an organic reaction forming an ether from organohalides and alcohol. 7. At room temperature ethers are pungent-smelling liquids.

**Ex. 4. Insert the necessary word.**

1. Ethers are organic compounds that contain an ... atom connected to two alkyl or aryl groups. 2. One of the most common ethers is ... ether. 3. Ethers are generally colourless ...-smelling liquids at room temperature. 4. Hydrobromic and hydroiodic acids are especially useful for ether ..., because both are strong acids and their anions are good nucleophiles. 5. Ethers are frequently employed as inert ... in organic synthesis. 6. The solubility of ethers ... with an increase in the number of carbon atoms. 7. Ether is used as ... to prevent infection when an injection is administered.

cleavage, antiseptic, diethyl, decreases, oxygen, sweet, solvents
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## UNIT XII

# ALDEHYDES AND KETONES

Aldehydes and ketones are structurally very similar, both have a carbon-oxygen double bond often called a carbonyl group. Like any double bond, the carbonyl group is composed of a  $\sigma$  bond and a  $\pi$  bond, but unlike carbon-carbon double bonds it is polar due to oxygen's electronegativity.

Aldehydes and ketones differ in that aldehydes have at least one hydrogen atom bonded to the carbonyl group, whereas in ketones the carbonyl group has carbons bonded on each other.

Aldehydes and ketones are quite prevalent in nature. They appear as natural fragrances and flavorings. In addition, carbonyl groups and their derivatives are the main structural features of carbohydrates and appear as functional groups in other natural compounds including dyes, vitamins, and hormones.

Compounds with two aldehyde or two ketone groups are named *dials* and *diones*, respectively.

Aldehydes and ketones are structurally similar and consequently they show similar chemical properties. They do differ significantly in one chemical property – susceptibility to oxidation. Aldehydes are easily oxidized under mild conditions, ketones are not.

Aldehydes can be distinguished from ketones using Tollens' reagent which is a solution of silver nitrate in ammonium hydroxide. As the aldehyde is oxidized to the salt of a carboxylic acid, silver ion ( $\text{Ag}^+$ ) is reduced to metallic silver. Ketones give no reaction.

Aldehydes and ketones possess a carbon-oxygen double bond and, as we might expect, addition is their most characteristic chemical reaction.

Although aldehydes and ketones add a variety of reagents the reactions are generally not as simple as those of alkenes. This is because the product of straight addition is frequently unstable and either exists in equilibrium with the starting materials or reacts further to form a more stable substance.

Aldehydes and ketones generally react by a nucleophilic addition mechanism. In this type of mechanism a nucleophile (Lewis base) is attracted to and bonds to the partially positive carbonyl carbon. The reaction can be initiated by either an acid or base.

Addition of hydrogen to aldehydes and ketones, catalytically and under pressure, results in the formation of primary and secondary alco-

hols, respectively. The reaction and its mechanism are analogous to that of addition of hydrogen to alkenes. It does not involve nucleophilic addition as do other reactions of carbonyl compounds.

A second and often more convenient method for the reduction of aldehydes and ketones to alcohols involves the use of metal hydrides such as lithium aluminium hydride, or sodium borohydride. The procedure involves treating a carbonyl compound with lithium aluminium hydride in ether followed by hydrolysis in water or dilute acid.

Aldehydes and ketones are most easily prepared by the oxidation of alcohols, this is especially true for ketones of low molecular weight which may be prepared from inexpensive secondary alcohols.

Primary alcohols can sometimes be oxidized to aldehydes, although this is a delicate reaction since aldehydes are themselves easily oxidized. Special conditions are usually employed, such as dehydrogenation over copper at high temperatures. Aromatic aldehydes are conveniently produced by hydrolysis of 1,1-dichloro compounds. Both aldehydes and ketones can be formed by the action of ozone on alkenes. Ozonolysis, as this process is called, is useful not only in synthesizing aldehydes and ketones, but also in locating carbon-carbon double bonds.

An important reaction for synthesizing aromatic ketones involves the use of an acid chloride like acetyl chloride in the Friedel – Crafts reaction.

### Important aldehydes and ketones

*Acetone* (b. p.  $56^{\circ}\text{C}$ ), the simplest ketone, is an inexpensive industrial solvent. It is synthesized industrially using the oxidation of isopropyl alcohol. It can also be formed by fermentation of sugars or starch, and is found on the breath and in the urine of many sufferers of diabetes. Acetone is a super solvent. It can dissolve most organic compounds and is also miscible with water. Casual exposure to acetone poses no health risk. Acetone is highly volatile and is also highly flammable.

*Methyl and ethyl ketone* (b. p.  $80^{\circ}\text{C}$ ) shows many of acetone's desirable solvent properties and is used when a solvent with a higher boiling point is needed. It is approximately twice as expensive as acetone, however, in many processes the solvent is recovered and reused so that the greater initial expense is not especially important.

*Acetaldehyde* (b. p.  $20^{\circ}\text{C}$ ) is sweet smelling but narcotic. It is formed readily by the hydration of acetylene and is used mainly as a raw material for the synthesis of other organic compounds, among

them acetic acid, by reaction with oxygen. Chlorination of acetaldehyde gives chloral; chloral in the form of its hydrate is a hypnotic and is also used to prepare DDT. Acetaldehyde is present in ripe fruits, especially in apples and is a metabolite of ethanol. It is less toxic than formaldehyde.

*n-Butyraldehyde* (b. p. 75°C), formed from oxidation of *n*-butyl alcohol, is widely used in the production of safety glass.

From a commercial standpoint the simplest aldehyde, *formaldehyde*, is also the most important. Pure formaldehyde is a gas (b. p. 21°C), which can be neither readily isolated nor handled in this state. Formaldehyde is toxic, but useful. It kills viruses, fungi and bacteria, and is used to disinfect and sterilize equipment. The largest commercial use of formaldehyde is in the preparation of phenol-formaldehyde resins for molded articles and for use in plywood. These resins are thermosetting; this means that in the course of the manufacture of an article the phenol-formaldehyde resin melts and then, under the influence of heat and pressure, resolidifies to become permanently infusible. The properties of thermosetting polymers contrast with those of thermoplastic polymers. The latter, which include most vinyl polymers, are solids at room temperature but can be molded at higher temperatures. This fusion-solidification process can be repeated numerous times.

Formaldehyde is prepared from controlled oxidation of methanol over a metal catalyst and is sold as a 37% solution in water (formalin) and also as a solid polymer, *paraformaldehyde*, from which it can be recovered by heating. Candles of paraformaldehyde are used as fumigating agents.

Since formaldehyde can be produced inexpensively and polymerizes readily (to paraformaldehyde), a great deal of effort has gone into investigations of its use in the preparation of commercial polymers.

The problem in using pure *polyformaldehyde* has been to prevent its decomposition to formaldehyde, which is poisonous. It can be shown that the decomposition begins at the ends of the chains, but when these free hydroxyl groups are converted into ester groups a stable polymer results.

Formaldehyde and ammonia react to form the cage-like compound *hexamethylenetetramine*, which liberates formaldehyde upon treatment with acid. Hexamethylenetetramine is medicinally useful as a urinary antiseptic (urotropine) and is also oxidized by nitric acid to the important military explosive cyclonite.

## Properties of aldehydes and ketones

**Physical properties.** The physical properties of aldehydes and ketones are described as follows. Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature. The boiling points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to the absence of intermolecular hydrogen bonding.

The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bonds with water.

However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc. The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

**Chemical properties.** Aldehydes and ketones are created by the mild oxidation of primary and secondary alcohols.

Chemically aldehydes and ketones both contain a carbonyl carbon and thus have similar chemical reactivities. However, aldehydes are more susceptible to oxidation because of the hydrogen atom attached to the carbonyl group. This is the basis for distinguishing between these two classes of compounds.

### REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. What is the difference between aldehydes and ketones? 2. How are primary and secondary alcohols formed from aldehydes and ketones? 3. How are aldehydes and ketones formed? 4. What are the most important aldehydes and ketones? 5. Where are aldehydes and ketones soluble? 6. What does the odour of the lower aldehydes and ketones depend on? 7. What is the basis for distinguishing between aldehydes and ketones?

**Ex. 2. Match the words with their definitions.**

- |                     |  |
|---------------------|--|
| 1) dione            | a) a solution of silver nitrate in ammonium hydroxide                  |
| 2) acetone          | b) a compound which has one hydrogen atom bonded to the carbonyl group |
| 3) ozonolysis       | c) a compound with two aldehyde or two ketone groups                   |
| 4) primary alcohols | d) a substance which can accept hydrogen ions (protons)                |
| 5) Tollens' reagent | e) a compound in which the carbon atom is attached to one alkyl group  |
| 6) aldehyde         | f) the action of ozone on alkenes                                      |
| 7) base             | g) the simplest ketone 2-propanone                                     |

**Ex. 3. Say whether the following statements are true or false.**

1. Aldehydes and ketones are structurally similar and they show similar chemical reactions. 2. Ketones are easily oxidized under mild conditions, aldehydes are not. 3. Ketones have at least one hydrogen atom bonded to the carbonyl group. 4. Aldehydes and ketones generally react by a nucleophilic addition mechanism. 5. Aldehydes and ketones are most easily prepared by the oxidation of water. 6. Acetone is highly volatile and is also highly flammable. 7. Solubility of aldehydes and ketones increases rapidly on increasing the length of alkyl chain.

**Ex. 4. Insert the necessary word.**

1. Aldehydes and ketones both have a carbon-oxygen double bond often called a ... group. 2. ... is the most characteristic chemical reaction of aldehydes and ketones. 3. A more convenient method for the reduction of aldehydes and ketones to ... involve the use of metal hydrides. 4. Both aldehydes and ketones can be formed by the action of ... on alkenes. 5. Acetone can be formed by fermentation of ... or starch. 6. The lower aldehydes have ... odour. 7. Aldehydes are more susceptible to ... because of the hydrogen atom attached to the carbonyl group.

alcohols, oxidation, ozone, carbonyl, pungent/sharp, addition, sugars
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## UNIT XIII

# CARBOXYLIC ACID

Carboxylic acid is any of a class of organic compounds in which a carbon (C) atom is bonded to an oxygen (O) atom by a double bond and to a hydroxyl group ( $\text{-OH}$ ) by a single bond. A fourth bond links the carbon atom to a hydrogen (H) atom or to some other univalent combining group. The carboxyl ( $\text{COOH}$ ) group is so-named because of the carbonyl group ( $\text{C=O}$ ) and hydroxyl group.

The chief chemical characteristic of the carboxylic acids is their acidity. They are generally more acidic than other organic compounds containing hydroxyl groups but are generally weaker than the familiar mineral acids (e. g., hydrochloric acid,  $\text{HCl}$ , sulfuric acid,  $\text{H}_2\text{SO}_4$ , etc.).

Carboxylic acids occur widely in nature. The fatty acids are components of glycerides, which in turn are components of fat. Hydroxyl acids, such as lactic acid (found in sour-milk products) and citric acid (found in citrus fruits), and many keto acids are important metabolic products that exist in most living cells. Proteins are made up of amino acids, which also contain carboxyl groups.

Compounds in which the  $\text{-OH}$  of the carboxyl group is replaced by certain other groups are called carboxylic acid derivatives, the most important of which are acyl halides, acid anhydrides, esters, and amides.

Carboxylic acid derivatives have varied applications. For example, in addition to its use as a disinfectant, formic acid, the simplest carboxylic acid, is employed in textile treatment and as an acid reducing agent. Acetic acid is extensively used in the production of cellulose plastics and esters. Aspirin, the ester of salicylic acid, is prepared from acetic acid. Palmitic acid and stearic acid are important in the manufacture of soaps, cosmetics, pharmaceuticals, candles, and protective coatings. Stearic acid also is used in rubber manufacture. Acrylic acid is employed as an ester in the production of polymers (long-chain molecules) known as acrylates. Methacrylic acid serves as an ester and is polymerized to form Lucite. Oleic acid is used in the manufacture of soaps and detergents and of textiles.

### Properties of carboxylic acids

**Acidity.** The most important property of carboxylic acids, and the one that is responsible for naming them such, is their acidity. Carboxylic acids are said to be strong acids, even though they are much weaker than the most important mineral acids – sulfuric ( $\text{H}_2\text{SO}_4$ ), nitric ( $\text{HNO}_3$ ), and hydrochloric ( $\text{HCl}$ ).

**Solubility.** The solubility of carboxylic acids in water is similar to that of alcohols, aldehydes, and ketones. Acids with fewer than about five carbons dissolve in water; those with a higher molecular weight are insoluble owing to the larger hydrocarbon portion, which is hydrophobic. The sodium, ammonium, and potassium salts of carboxylic acids, however, are generally quite soluble in water.

**Boiling point.** Carboxylic acids have much higher boiling points than hydrocarbons, alcohols, ethers, aldehydes, or ketones of similar molecular weight. Carboxylic acids with higher molecular weights are solids at room temperature (e. g., benzoic and palmitic acids). Virtually all salts of carboxylic acids are solids at room temperature, as can be expected for ionic compounds.

**Odour.** Unbranched-chain carboxylic acids (fatty acids) that are liquids at room temperature, especially those from propanoic ( $C_3$ ) to decanoic ( $C_{10}$ ) acid, have very foul, disagreeable odours. An example is butanoic (butyric) acid ( $C_4$ ), which is the main ingredient in stale perspiration and thus the chief cause of “locker-room” odour.

### Classes of carboxylic acids

**Saturated aliphatic acids.** Formic acid,  $HCOOH$ , is found not only in ants but also in the droplets on the tiny hairs of the stinging nettle plant (in the family *Urticaceae*), and the acidity of this compound causes the stinging sensation felt when these hairs are touched.

Acetic acid,  $CH_3COOH$ , has been known to humankind for thousands of years (at least in water solution). It is the compound that gives the sourness to vinegar and is produced by the bacterial oxidation of ethanol in wine. Household vinegar contains about five percent acetic acid. Acetic acid is important in the metabolic processes of humans and, indeed, of all animals and plants.

The even-numbered fatty acids from 4 to 10 carbon atoms are mostly found in milkfats (cow’s milk, goat’s milk, some hard cheeses). The higher even-numbered saturated acids, from  $C_{12}$  to  $C_{18}$  (lauric, myristic, palmitic, and stearic), are present in the fats and oils of many animals and plants, with palmitic and stearic acids being the most prevalent. Lauric acid ( $C_{12}$ ) is the main acid in coconut oil (45–50%) and palm kernel oil (45–55%). Nutmeg butter is rich in myristic acid ( $C_{14}$ ), which constitutes 60–75% of the fatty-acid content. Palmitic acid ( $C_{16}$ ) constitutes between 20 and 30% of most animal fats and is also an important constituent of most vegetable fats (35–45% of palm oil). Stearic

acid (C<sub>18</sub>) is also present in most fats but usually in smaller amounts than palmitic. Cocoa butter is unusually rich in stearic acid (35%).

Even-numbered saturated fatty acids higher than C<sub>18</sub> are much less common in fats but do occur in some waxes (e. g., beeswax). Odd-numbered fatty acids have been found only in trace amounts in natural compounds, but many have been produced synthetically in the laboratory.

**Unsaturated aliphatic acids.** A number of acids important in organic chemistry contain carbon-carbon double bonds. There exist  $\alpha$ -,  $\beta$ -unsaturated acids, in which the double bond is between the second and third carbons of the chain, as well as unsaturated acids, in which the double bond occurs in other positions. Although many of these latter acids occur in nature, they are less easy to synthesize than  $\alpha$ -,  $\beta$ -unsaturated acids. Many unsaturated acids occur in fats.

Unsaturated acids exhibit chemical properties expected of compounds that contain both a COOH group and one or more carbon-carbon double bonds. Like all carboxylic acids, they are acidic; can be reduced to alcohols; can be converted to acid derivatives; and, like other compounds containing double bonds, can undergo the normal double-bond addition reactions and oxidation-reduction reactions.

**Aromatic acids.** Aromatic acids include compounds that contain a COOH group bonded to an aromatic ring. The simplest aromatic acid is benzoic acid. Some other important aromatic acids include the following: salicylic acid, gallic acid, phenylacetic acid, mandelic acid, cinnamic acid and many others.

**Polycarboxylic acids.** Unbranched-chain dicarboxylic acids contain two COOH groups. As a result they can yield two kinds of salts. Because one COOH group is still present in the compound, it has the properties of both a salt and an acid. The two most important unsaturated dicarboxylic acids are fumaric and maleic acids. Malic acid is found in many fruits, including apples. Fumaric acid is found in bolete mushrooms, lichen and Iceland moss. Human skin naturally produces fumaric acid when exposed to sunlight.

**Amino acids.** Compounds containing both a carboxyl group and an amino group are called amino acids. Twenty of these are found in proteins, all of which are  $\alpha$ -amino acids.

### Synthesis of carboxylic acids

Most of the methods for the synthesis of carboxylic acids can be put into one of two categories: (1) hydrolysis of acid derivatives and (2) oxidation of various compounds.

**Hydrolysis of acid derivatives.** All acid derivatives can be hydrolyzed (cleaved by water) to yield carboxylic acids; the conditions required range from mild to severe, depending on the compound involved.

**Oxidation.** The oxidation of primary alcohols is a common method for the synthesis of carboxylic acids. This requires a strong oxidizing agent, the most common being chromic acid ( $\text{H}_2\text{CrO}_4$ ), potassium permanganate ( $\text{KMnO}_4$ ), and nitric acid ( $\text{HNO}_3$ ).

**Other synthetic methods.** Grignard reagents react with carbon dioxide (either in the gaseous form, which is bubbled through the solution, or as the solid dry ice) to give magnesium salts of carboxylic acids, which are converted to the acids themselves upon treatment with acid. Other methods for the synthesis of carboxylic acids include the malonic ester synthesis, the haloform reaction, and the Cannizzaro reaction.

## REVISION EXERCISES

### Ex. 1. Answer the following questions.

1. What is carboxylic acid? Why was it so named? 2. Where do carboxylic acids occur in nature? 3. What are carboxylic acid derivatives? Where can they be found? 4. What is the most important property of carboxylic acids? 5. Do carboxylic acids dissolve in water? 6. How does the butanoic acid smell? 7. How many classes of carboxylic acids are there? 8. Why is acetic acid so important? Where can it be found? 9. What are the most widely used ways of synthesis of carboxylic acids?

### Ex. 2. Match the words with their definitions.

- |                       |  |
|-----------------------|--|
| 1) metabolic products | a) to give something in order to help  |
| 2) acid               | b) a smell, especially an unpleasant one   |
| 3) beeswax            | c) any of the sequences of biochemical reactions, catalysed by enzymes, that occur in all living cells: concerned mainly with the exchange of energy and chemicals |
| 4) donate             | d) a number that cannot be divided exactly by two, for example 1   |
| 5) odour              | e) any chemical reaction in which the oxidation number of a participating chemical species changes   |

- |                                 |  |
|---------------------------------|--|
| 6) odd number                   | f) a chemical substance that has a pH of less than 7; strong ones can burn holes in material or damage your skin |
| 7) oxidation-reduction reaction | g) any of a class of chemical reactions in which an atom or group of atoms is added to a molecule                |
| 8) treatment                    | h) a substance produced by bees, used especially for making furniture polish and candles                         |
| 9) addition reaction            | i) technologies that use chemicals to process materials or wastes.   |

**Ex. 3. Say whether the following statements are true or false.**

1. Proteins are made up of aldehydes and ketones, which also contain carboxyl groups. 2. Acyl halides, acid anhydrides, esters, and amides are the most important carboxylic acid derivatives. 3. Aspirin is prepared from carboxylic acid derivative. 4. Names of many simple carboxylic acids reflect the names of the sources they were originally isolated. 5. When common names are used, substituents on the hydrocarbon chain are designated by Greek numbers rather than by letters. 6. Acids with fewer than about five carbons are hardly dissolved in water. 7. Boiling a carboxylic acid requires more heat than boiling the corresponding alcohol. 8. People consume some carboxylic acids every morning.

**Ex. 4. Insert the necessary word.**

1. At present, 30 elements are definitely known ... to human life. 2. The most abundant elements are hydrogen, carbon, nitrogen, and oxygen; sodium, magnesium, potassium, calcium, phosphorus, sulfur, and chlorine are also present ... . 3. Although present only in trace amounts, the first-row transition metals are essential for the action of ... (biological catalysts). In time, other elements will probably be found to be essential. 4. Life is organized around the functions of ..., the smallest unit in living things that exhibits the properties normally associated with life, such as reproduction, ..., mutation, and sensitivity to external stimuli. 5. As the fundamental building blocks of all living systems, aggregates of cells form ..., which in turn are assembled into the organs that make up complex living systems. 6. Therefore, to understand how life is ..., we must learn how cells operate on the molecular level. This is the main thrust of biochemistry.

maintained and reproduced, in relatively large amounts, to be essential, the cell, metabolism, tissues, many enzymes
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## UNIT XIV

### ESTERS

Esters are chemical compounds derived from an acid (organic or inorganic) in which at least one –OH (hydroxyl) group is replaced by an –O– alkyl (alkoxy) group. Esters derived from carboxylic acids are the most common. The general formula is RCOOR' (R and R' are any organic combining groups). The term *ester* was introduced in the first half of the 19<sup>th</sup> century by German chemist Leopold Gmelin.

**Nomenclature.** Ester names are derived from the parent alcohol and the parent acid, where the latter may be organic or inorganic. Esters derived from the simplest carboxylic acids are commonly named according to the more traditional, so-called “trivial names”, e. g. formate, acetate, propionate, and butyrate, as opposed to the IUPAC nomenclature methanoate, ethanoate, propanoate and butanoate. Esters derived from more complex carboxylic acids are, on the other hand, more frequently named using the systematic IUPAC name, based on the name for the acid followed by the suffix *-oate*, for example, hexyl octanoate. Cyclic esters are called lactones, regardless of whether they are derived from an organic or an inorganic acid. One example of a (organic) lactone is *gamma*-valerolactone.

The names can also be derived from an inorganic acid and an alcohol. Thus, the nomenclature extends to inorganic oxo acids, e. g. phosphoric acid, sulfuric acid, nitric acid and boric acid. For example, triphenyl phosphate is the ester derived from phosphoric acid and phenol. Organic carbonates are derived from carbonic acid; for example, ethylene carbonate is derived from carbonic acid and ethylene glycol.

**Physical properties.** Esters contain a carbonyl center, which gives rise to 120° C–C–O and O–C–O angles. Unlike amides, esters are structurally flexible functional groups because rotation about the C–O–C bonds has a low barrier. Their flexibility and low polarity is manifested in their physical properties; they tend to be less rigid (lower melting point) and more volatile (lower boiling point) than the corresponding amides.

Esters are more polar than ethers but less polar than alcohols. They have dipole-dipole interactions as well as van der Waals dispersion forces. Their boiling points are not high. They participate in hydrogen bonds as hydrogen-bond acceptors, but cannot act as hydrogen-bond donors, unlike their parent alcohols. Because of their lack of hydrogen-

bond-donating ability, esters do not self-associate. The ability to participate in hydrogen bonding confers some water solubility. But solubility decreases with the chain length. The reason for the solubility is that although esters can't hydrogen bond with themselves, they can hydrogen bond with water molecules.

**Preparation.** Esterification is the classic synthesis for ester preparation. It involves treating a carboxylic acid with an alcohol in the presence of a dehydrating agent. In the reaction the hydroxyl group (OH) of the carboxylic acid is replaced by the alkoxy group (R'O) of the alcohol. The reaction is slow in the absence of a catalyst. Sulfuric acid is a typical catalyst for this reaction. Many other acids are also used such as polymeric sulfonic acids. Since esterification is highly reversible, the yield of the ester can be improved using Le Chatelier's principle:

- using the alcohol in large excess (i. e., as a solvent);
- using a dehydrating agent: sulfuric acid not only catalyzes the reaction but sequesters water (a reaction product). Other drying agents such as molecular sieves are also effective;
- removal of water by physical means such as distillation.

The reverse of the esterification reaction is an example of hydrolysis. Esters may also be obtained by reaction of acid halides or acid anhydrides with alcohols or by reaction of salts of carboxylic acids with alkyl halides. One ester may be converted to another ester by reaction with an alcohol, a carboxylic acid, or a third ester in the presence of a catalyst. The hydrolysis of esters in the presence of alkalies, a reaction called saponification, is utilized in the preparation of soaps from fats and oils and is also used for the quantitative estimation of esters.

**Applications.** Esters are widespread in nature and are widely used in industry. They are responsible for the aroma of many fruits, including apples, durians, pears, bananas, pineapples, and strawberries.

Esters of low molecular weight are colourless, volatile liquids with pleasant odours, slightly soluble in water. They are commonly used as fragrances and found in essential oils and pheromones. Many are responsible for the fragrance and flavour of flowers and fruits; for example, isopentyl acetate is present in bananas, methyl salicylate in wintergreen, and ethyl butyrate in pineapples. These and other volatile esters with characteristic odours are used in synthetic flavours, perfumes, and cosmetics. Certain volatile esters are used as solvents for lacquers, paints, and varnishes; for this purpose, large quantities of ethyl acetate and butyl acetate are commercially produced. Waxes secreted by animals

and plants are esters formed from long-chain carboxylic acids and long-chain alcohols. Fats and oils are esters of long-chain carboxylic acids and glycerol. Glycerides, which are fatty acid esters of glycerol, are important esters in biology, being one of the main classes of lipids, and making up the bulk of animal fats and vegetable oils.

Liquid esters of low volatility serve as softening agents for resins and plastics. Esters also include many industrially important polymers. Polymethyl methacrylate is a glass substitute sold under the names Lucite and Plexiglas; polyethylene terephthalate is used as a film (Mylar) and as textile fibres sold as Terylene, Fortrel, and Dacron. Several billion kilograms of polyesters are produced industrially annually, important products being polyethylene terephthalate, acrylate esters, and cellulose acetate.

Nitrate esters (e. g., glyceryl trinitrate, or nitroglycerin) are explosive. Phosphate esters are biologically important (nucleic acids belong to this group) forming the backbone of DNA. They are used widely in industry as solvents, plasticizers, flame retardants, gasoline and oil additives, and insecticides.

Esters of sulfuric and sulfurous acids are used in the manufacture of dyes and pharmaceuticals. Dimethyl sulfate, the best-known ester of sulfuric acid, is a dangerous poison.

### REVISION EXERCISES

#### **Ex. 1. Answer the following questions.**

1. When was the term “ester” introduced? 2. What esters are the most common? 3. What are the names of cyclic esters derived from? 4. What influences the decrease of solubility of esters? 5. Are esters soluble in water? Why? 6. What is the classic synthesis for ester preparation? 7. What catalysts are used for ester preparation?

#### **Ex. 2. Match the words with their definitions.**

- |                 |  |
|-----------------|--|
| 1) acid         | a) a compound that contributes to the flavors and aromas in fruits and flowers   |
| 2) nomenclature | b) a method of separating mixtures based on differences in their volatilities in a boiling liquid mixture  |
| 3) ester        | c) alkaline hydrolysis of the fatty acid esters  |
| 4) amide        | d) a chemical substance whose aqueous solutions are characterized by sour taste; the ability to turn blue litmus red and the ability to react with bases |

- 5) polarity e) a system of names or terms or the rules for forming these terms
- 6) distillation f) a separation of electric charge leading to a molecule or its chemical groups having an electric dipole or multiple moment
- 7) saponification g) functional group containing a carbonyl group linked to a nitrogen atom

**Ex. 3. Say whether the following statements are true or false.**

1. Esters are chemical compounds derived from an organic or inorganic acid. 2. Esters derived from the simplest carboxylic acids are commonly named using the systematic IUPAC names. 3. Esters contain a chiral centre which gives rise to  $120^\circ$  C–C–O and O–C–O angles. 4. Esters are more polar than ethers but are less polar than alcohols. 5. Esters participate in hydrogen bonds as hydrogen-bond acceptors. 6. Esters can't hydrogen bond with water molecules. 7. Esters are responsible for the aroma of many fruits.

**Ex. 4. Insert the necessary word.**

1. Ester names are derived from the parent ... and the parent acid. 2. Flexibility and low ... of esters is manifested in their physical properties. 3. Esters cannot act as hydrogen-bond ... unlike their parent alcohols. 4. ... is the classic synthesis for ester preparation. 5. Sulfuric acid is a typical ... for the reaction of esterification. 6. Esters are commonly used as ... and found in essential oils and pheromones. 7. Fats and oils are ... of long-chain carboxylic acids and glycerol.

esterification, polarity, esters, catalysts, alcohol, fragrances, donors

# UNIT XV

## CARBOHYDRATES

Carbohydrates (also called saccharides) are molecular compounds made from just three elements: carbon, hydrogen and oxygen. Monosaccharides (e. g. glucose) and disaccharides (e. g. sucrose) are relatively small molecules. They are often called sugars. Other carbohydrate molecules are very large (polysaccharides such as starch and cellulose).

Carbohydrates are:

- a source of energy for the body, e. g. glucose and a store of energy, e. g. starch in plants;
- building blocks for polysaccharides (giant carbohydrates), e. g. cellulose in plants and glycogen in the human body;
- components of other molecules, e. g. DNA, RNA, glycolipids, glycoproteins, etc.

*Monosaccharides* are the simplest carbohydrates and are often called single sugars. They are the building blocks from which all bigger carbohydrates are made.

Monosaccharides have the general molecular formula  $(\text{CH}_2\text{O})_n$ , where  $n$  can be 3, 5 or 6. They can be classified according to the number of carbon atoms in a molecule:

$n = 3$  – trioses, e. g. glyceraldehyde;

$n = 5$  – pentoses, e. g. ribose and deoxyribose ('pent' indicates 5);

$n = 6$  – hexoses, e. g. fructose, glucose and galactose ('hex' indicates 6).

There is more than one molecule with the molecular formula  $\text{C}_5\text{H}_{10}\text{O}_5$  and more than one with the molecular formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . Molecules that have the same molecular formula but different structural formulae are called structural isomers.

Glyceraldehyde's molecular formula is  $\text{C}_3\text{H}_6\text{O}_3$ . Its structural formula shows it contains an aldehyde group ( $-\text{CHO}$ ) and two hydroxyl groups ( $-\text{OH}$ ). The presence of an aldehyde group means that glyceraldehyde can also be classified as an aldose. It is a reducing sugar and gives a positive test with Benedict's reagent.

Pentoses and hexoses can exist in two forms: cyclic and non-cyclic. In the non-cyclic form their structural formulae show they contain either an aldehyde group or a ketone group.

Monosaccharides containing the aldehyde group are classified as aldoses, and those with a ketone group are classified as ketoses. Aldoses

are reducing sugars; ketoses are non-reducing sugars. This is important in understanding the reaction of sugars with Benedict's reagent.

*Glucose* is the most important carbohydrate fuel in human cells. Its concentration in the blood is about  $1 \text{ gdm}^{-3}$ . The small size and solubility in water of glucose molecules allows them to pass through the cell membrane into the cell.

There are two forms of the cyclic glucose molecule:  $\alpha$ -glucose and  $\beta$ -glucose. Two glucose molecules react to form the disaccharide maltose. Starch and cellulose are polysaccharides made up of glucose units.

*Galactose* molecules look very similar to glucose molecules. They can also exist in  $\alpha$ - and  $\beta$ -forms.

*Fructose*, glucose and galactose are all hexoses. However, whereas glucose and galactose are aldoses (reducing sugars), fructose is a ketose (a non-reducing sugar). It also has a five-atom ring rather than a six-atom ring. Fructose reacts with glucose to make the disaccharide sucrose.

*Ribose and deoxyribose* are pentoses. The ribose unit forms part of a nucleotide of RNA. The deoxyribose unit forms part of the nucleotide of DNA.

Monosaccharides are rare in nature. Most sugars found in nature are *disaccharides*. These form when two monosaccharides react.

A condensation reaction takes place releasing water. This process requires energy. A glycosidic bond forms and holds the two monosaccharide units together.

The three most important disaccharides are sucrose, lactose and maltose. They are formed from the  $\alpha$  forms of the appropriate monosaccharides. Sucrose is a non-reducing sugar. Lactose and maltose are reducing sugars.

Disaccharides are soluble in water, but they are too big to pass through the cell membrane by diffusion. They are broken down in the small intestine during digestion to give the smaller monosaccharides that pass into the blood and through cell membranes into cells.

Monosaccharides are used very quickly by cells. However, a cell may not need all the energy immediately and it may need to store it. Monosaccharides are converted into disaccharides in the cell by condensation reactions. Further condensation reactions result in the formation of polysaccharides. These are giant molecules which, importantly, are too big to escape from the cell. These are broken down by hydrolysis into monosaccharides when energy is needed by the cell.

Monosaccharides can undergo a series of condensation reactions, adding one unit after another to the chain until very large molecules (*polysaccharides*) are formed. This is called condensation polymerisation, and the building blocks are called monomers. The properties of a polysaccharide molecule depend on:

- its length (though they are usually very long);
- the extent of any branching (addition of units to the side of the chain rather than one of its ends);
- any folding which results in a more compact molecule;
- whether the chain is 'straight' or 'coiled'.

*Starch* is often produced in plants as a way of storing energy. It exists in two forms: amylose and amylopectin. Both are made from  $\alpha$ -glucose. Amylose is an unbranched polymer of  $\alpha$ -glucose. The molecules coil into a helical structure. It forms a colloidal suspension in hot water. Amylopectin is a branched polymer of  $\alpha$ -glucose. It is completely insoluble in water.

*Glycogen* is amylopectin with very short distances between the branching side-chains. Starch from plants is hydrolysed in the body to produce glucose. Glucose passes into the cell and is used in metabolism. Inside the cell, glucose can be polymerised to make glycogen which acts as a carbohydrate energy store.

*Cellulose* is a third polymer made from glucose. But this time it's made from  $\beta$ -glucose molecules and the polymer molecules are 'straight'.

Cellulose serves a very different purpose in nature to starch and glycogen. It makes up the cell walls in plant cells. These are much tougher than cell membranes. This toughness is due to the arrangement of glucose units in the polymer chain and the hydrogen-bonding between neighbouring chains.

Cellulose is not hydrolysed easily and, therefore, cannot be digested so it is not a source of energy for humans. The stomachs of Herbivores contain a specific enzyme called cellulase which enables them to digest cellulose.

### Carbohydrate benefits

The right kind of carbohydrates can be incredibly good for you. Not only are they necessary for your health, but they carry a variety of added benefits.

**Mental health.** Carbohydrates may be important to mental health. A study published in 2009 in the journal JAMA Internal Medicine found that people on a high-fat, low-carbohydrates diet for a year had

more anxiety, depression and anger than people on a low-fat, high-carbohydrates diets. Scientists suspect that carbohydrates help with the production of serotonin in the brain.

Carbohydrates may help memory, too. A 2008 study at Tufts University had overweight women cut carbohydrates entirely from their diets for one week. Then, they tested the women's cognitive skills, visual attention and spatial memory. The women on low-carbohydrates diets did worse than overweight women on low-calorie diets that contained a healthy amount of carbohydrates.

**Weight loss.** Though carbohydrates are often blamed for weight gain, the right kind of carbohydrates can actually help you lose and maintain a healthy weight. This happens because many good carbohydrates, especially whole grains and vegetables with skin, contain fiber. It is difficult to get sufficient fiber on a low-carbohydrates diet. Dietary fiber helps you to feel full, and generally comes in relatively low-calorie foods.

A study published in the *Journal of Nutrition* in 2009 followed middle-age women for 20 months and found that participants who ate more fiber lost weight, while those who decreased their fiber intake gained weight. Another recent study linked fat loss with low-fat diets, not low-carbohydrates ones.

**Good source of nutrients.** Whole, unprocessed fruits and vegetables are well known for their nutrient content. Some are even considered superfoods because of it – and all of these leafy greens, bright sweet potatoes, juicy berries, tangycitruses and crunchy apples contain carbohydrates.

One important, plentiful source of carbohydrates is whole grains. A large study published in 2010 in the *Journal of the American Dietetic Association* found that those eating the most whole grains had significantly higher amounts of fiber, energy and polyunsaturated fats, as well as all micronutrients (except vitamin B12 and sodium). An additional study, published in 2014 in the journal *Critical Reviews in Food Science and Nutrition*, found that whole grains contain antioxidants, which were previously thought to exist almost exclusively in fruits and vegetables.

## REVISION EXERCISES

### **Ex. 1. Answer the following questions.**

1. What are carbohydrates? 2. What functions do carbohydrates perform? 3. What are structural isomers? 4. What is the difference

between aldoses and ketoses? 5. What do the properties of a polysaccharide molecule depend on? 6. What are the carbohydrate benefits for mental health? 7. What did a large study published in 2010 in the Journal of the American Dietetic Association find? 8. What did an additional study, published in 2014 in the journal Critical Reviews in Food Science and Nutrition discover?

**Ex. 2. Match the words with their definitions.**

- |                       |  |
|-----------------------|--|
| 1) sugar              | a) the process of breathing  |
| 2) Benedict's reagent | b) a substance that carries genetic information in the cells of the body   |
| 3) fuel               | c) to divide into parts or categories or to separate (as a chemical compound) into simpler substances                              |
| 4) respiration        | d) a sweet white or brown substance that is obtained from plants and used to make food and drinks sweet                            |
| 5) RNA                | e) to be the cause of (a situation, action, or state of mind)  |
| 6) DNA                | f) is a polymeric molecule implicated in various biological roles in coding, decoding, regulation, and expression of genes         |
| 7) break down         | g) a chemical commonly used to detect presence of reducing sugars, however other reducing substances also give a positive reaction |
| 8) result in          | h) a substance such as coal, gas, or oil that can be burned to produce heat or energy  |

**Ex. 3. Say whether the following statements are true or false.**

1. Monosaccharides and disaccharides are often called sugars.
2. Monosaccharides have the general molecular formula  $(\text{CH}_2\text{O})_n$ , where  $n$  can be 2, 4 or 8.
3. Monosaccharides containing the aldehyde group are classified as ketoses.
4. The most important carbohydrate fuel in human cells releases energy when the molecules are metabolized.
5. Fructose reacts with glucose to make the disaccharide lactose.
6. Most sugars found in nature are monosaccharides.
7. The women's cognitive skills, visual attention and spatial memory are better if they consume a healthy amount of carbohydrates every day.

**Ex. 4. Insert the necessary word.**

1. Starch is manufactured in the green leaves of plants from excess glucose produced during ... .
2. It serves the plant as ... .
3. Starch is

stored in chloroplasts in the form of granules and in such organs as ... of the tapioca plant; ... of the potato; ... pith of sago; and ... of corn, wheat, and rice. 4. When required, starch is broken down, in the presence of certain ... and water, into its constituent monomer glucose units, which diffuse from the cell ... the plant tissues. 5. In humans and other animals, starch is broken down into its ... sugar molecules, which then supply energy to the ... .

the roots, tissues, photosynthesis, the tuber, constituent, to nourish, a reserve, food supply, the seeds, enzymes

# UNIT XVI

## FATS

Fats occur naturally in food and play a significant role in human nutrition. Fats are used to store energy in the body, insulate body tissues, cushion internal organs, and transport fat-soluble vitamins in the blood. Fats also play an important role in food preparation: They enhance food flavor and food texture, make baked products tender, and conduct heat during cooking.

Fats are the most prevalent class of compounds (in living systems) referred to as lipids. Lipids are cellular compounds that are insoluble in water. Fats are soft, low-melting solids, with a density less than that of water. They have a greasy feel and are slippery. Because fats are insoluble in water and less dense than water, after meat that has a lot of fat in it has been cooked, upon cooling a layer of fat often appears on top of the juices. Fats and closely related oils are mixtures of compounds consisting of fatty acids combined with glycerol (commonly known as glycerin) via ester linkages. Fatty acids are long, straight chain carboxylic acids. A fat (or oil) is formed when three fatty acid molecules react with a glycerol molecule to yield a triglyceride (and three water molecules). Fats in the body are transported and stored as triglycerides.

Fat molecules are characterized as monoglycerides, diglycerides, or triglycerides, depending on whether there are one, two, or three fatty acid chains present in the molecules. Fatty acids in nature generally have an even number of carbon atoms because they are synthesized in cells via successive additions of two-carbon acetate groups in a step-wise cyclic reaction.

### Fats and oils

Dietary fats and oils are both triglycerides. Fats are generally solids and oils are generally liquids at ordinary room temperatures. The characteristics of fats and oils are related to the properties of the fatty acids that they contain. The larger the number of carbon atoms, the higher the melting point; the larger the number of double bonds, the lower the melting point. Oils contain a higher percentage of unsaturated fatty acids than fats. Fats from animal sources tend to be solids and fats from vegetable sources tend to be liquids. Thus fats are often referred to as “animal fats” and “vegetable oils”.

When fats or oils are exposed to air, they react with the oxygen or water vapor to form short-chain carboxylic acids. The short-chain acids are volatile and have unpleasant smells and tastes. For example, the strong smell and sour taste of vinegar are due to acetic acid, a two-carbon carboxylic acid. The oxidation process is called rancidification and can make foods unpalatable. The characteristic smell of rancid butter is due to the presence of butyric acid (a four-carbon acid). (Rancidity can also be the result of the hydrolysis of fats or oils.)

### **Saturated and unsaturated fatty acids**

When the fatty-acid molecule contains the maximum of hydrogen possible, the acid is said to be a saturated fatty acid. It is saturated with respect to hydrogen. Myristic, lauric, palmitic, and stearic acids are such saturated acids. They are solids at ordinary temperatures. When, however, the fatty-acid molecule does not contain the maximum amount of hydrogen possible, the acid is said to be an unsaturated fatty acid. It is unsaturated with respect to hydrogen. Such unsaturated acids are oleic, linolic, and linolenic acids. They are liquids at ordinary temperatures. By chemical means these acids may be made to take up, i. e., combine with, hydrogen. This process is known as hydrogenation. It converts a more unsaturated fatty acid into a less unsaturated one, or, if the hydrogenation is carried to completion, into a saturated fatty acid. Thus by hydrogenation oleic acid is converted into stearic acid. Linolic acid when hydrogenated can be made to take up twice as much hydrogen as oleic acid, and linolenic acid three times as much. Linolic acid is, therefore, a more highly unsaturated acid than oleic, while linolenic acid is more highly unsaturated than linolic.

Unsaturated fatty acids can be made to combine with other substances instead of with hydrogen. For example, they may be made to take up iodine or oxygen. Acids of a low degree of unsaturation, such as oleic acid, do not combine with oxygen with any great degree of acidity, but acids of a greater degree of unsaturation, such as linolic or linolenic, combine with it very readily; they do so merely upon exposure to the air.

### **Measures of unsaturation**

It is obvious, then, that it is important for industrial users of fats to know the degree of unsaturation of a given parcel of fat. This might be ascertained by determining the amount of hydrogen required to convert

it into a saturated fat. In practice this is a complicated procedure and so simpler methods are resorted to. The simplest of these is the determination of the amount of iodine that can be made to combine with the fat. The percentage by weight of iodine absorbed by the fat in the natural state is known as the *iodine number*. It is an index to the degree of unsaturation of the fat. The fats with the highest iodine numbers are the drying oils par excellence, linseed and tung oil, with which must also be classified menhaden fish oil.

### ◆ REVISION EXERCISES

#### Ex. 1. Answer the following questions.

1. What is the role of food in human nutrition? 2. What are the physical and chemical properties of fats? 3. What does the classification of fats depend on? 4. What is the difference between fats and oils? 5. What is the process of rancidification? 6. What is the difference between saturated and unsaturated fatty acids? 7. What is the iodine number?

#### Ex. 2. Match the words with their definitions.

- |                |  |
|----------------|--|
| 1) rancid      | a) oily in appearance, texture, or manner  |
| 2) greasy      | b) any of a class of often fragrant organic compounds represented by the formula $RCOOR$ and that are usually formed by the reaction between an acid and an alcohol with elimination of water  |
| 3) unpalatable | c) any of various substances that are soluble in non-polar organic solvents (as chloroform and ether), that are usually insoluble in water, that with proteins and carbohydrates constitute the principal structural components of living cells, and that include fats, waxes, phosphatides, cerebrosides, and related and derived compounds |
| 4) ester       | d) the act or process of nourishing or being nourished; specifically the sum of the processes by which an animal or plant takes in and utilizes food substances  |
| 5) lipid       | e) having a rank smell or taste usually from chemical change or decomposition  |
| 6) nutrition   | f) distasteful, disagreeable, unpleasant   |

**Ex. 3. Say whether the following statements are true or false.**

1. The percentage by weight of iodine absorbed by the fat in the natural state is known as the iodine number. 2. The fatty acids without carbon-carbon double bonds are classified as unsaturated, and those containing carbon-carbon double bonds are classified as saturated. 3. Unsaturated fatty acids can be made to combine with other substances instead of with oxygen. 4. Lipids are cellular compounds that are soluble in water. 5. The oleic, linolic, and linolenic acids are liquids at ordinary temperatures. 6. Fats and oils are practically always mixtures of triglycerids in varying proportions.

**Ex. 4. Insert the necessary word.**

1. There are about forty naturally ... fatty acids. 2. The fatty acids without carbon-carbon double bonds are classified as saturated, and those containing carbon-carbon double bonds are classified as ... . 3. Palmitic and stearic acids are the most common saturated fatty acids, and oleic and linoleic acids are the most common unsaturated fatty acids. 4. Oleic acid is monounsaturated because it has only one carbon-carbon double bond. 5. Linoleic, linolenic, and arachidonic acids are polyunsaturated because they have two, three, and four carbon-carbon double bonds, respectively. 6. A way to ... the relative degree of unsaturation of a fat or oil is to ... its iodine number. 7. The iodine number is the mass of iodine, in grams, that is consumed by (reacts with) 100 grams of a fat or oil. 8. Iodine ... with the carbon-carbon double bonds. 9. Thus the greater the number of double bonds, the higher the iodine number. 10. In general, fats have lower iodine numbers than oils because oils have greater ... of carbon-carbon bonds that are double bonds. 11. For example, ... iodine numbers for butter are 25 to 40, and for corn oil, 115 to 130.

typical, unsaturated, determine, measure, react, percentage, occurring
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## UNIT XVII

# PROTEINS AND PEPTIDES

Protein is a highly complex substance that is present in all living organisms. Proteins are of great nutritional value and are directly involved in the chemical processes essential for life. The importance of proteins was recognized by the chemists in the early 19<sup>th</sup> century who coined the name for these substances from the Greek *proteios*, meaning “holding first place”. Proteins are species-specific; that is, the proteins of one species differ from those of another species. They are also organ-specific; for instance, within a single organism, muscle proteins differ from those of the brain and liver.

A protein molecule is very large compared with molecules of sugar or salt and consists of many amino acids joined together to form long chains, much as beads are arranged on a string. There are about 20 different amino acids that occur naturally in proteins. Proteins of similar function have similar amino acid composition and sequence.

*Amino acid* is any of a group of organic molecules that consist of a basic amino group ( $-\text{NH}_2$ ), an acidic carboxyl group ( $-\text{COOH}$ ), and an organic R group (or side chain) that is unique to each amino acid.

Plants can synthesize all of the amino acids; animals cannot, even though all of them are essential for life. Plants can grow in a medium containing inorganic nutrients that provide nitrogen, potassium, and other substances essential for growth. They utilize the carbon dioxide in the air during the process of photosynthesis to form organic compounds such as carbohydrates. Animals, however, must obtain organic nutrients from outside sources. Nonruminant animals, including humans, obtain proteins principally from animals and their products – e. g., meat, milk, and eggs. The seeds of legumes are increasingly being used to prepare inexpensive protein-rich food.

Nowadays it is evident that protein molecules are produced in cells by the stepwise alignment of amino acids and are released into the body fluids only after synthesis is complete. And this process is impossible without enzymes, which are the catalysts of all metabolic reactions, enable an organism to build up the chemical substances necessary for life – proteins, nucleic acids, carbohydrates, and lipids – to convert them into other substances, and to degrade them. All enzymes identified thus far are proteins. Life without enzymes is not possible. There are several protein hormones with important regulatory func-

tions. In all vertebrates, the respiratory protein hemoglobin acts as oxygen carrier in the blood, transporting oxygen from the lung to body organs and tissues. A large group of structural proteins maintains and protects the structure of the animal body.

The common property of all proteins is that they consist of long chains of  $\alpha$ -amino (alpha amino) acids. In protein molecules the  $\alpha$ -amino acids are linked to each other by peptide bonds between the amino group of one amino acid and the carboxyl group of its neighbor.

Proteins usually are almost neutral molecules; that is, they have neither acidic nor basic properties.

Biochemists often refer to four distinct aspects of a protein's structure:

*Primary structure*: the amino acid sequence. A protein is a polyamide.

*Secondary structure*: regularly repeating local structures stabilized by hydrogen bonds. The most common examples are the alpha helix, beta sheet and turns. Because secondary structures are local, many regions of different secondary structure can be present in the same protein molecule.

*Tertiary structure*: the overall shape of a single protein molecule; the spatial relationship of the secondary structures to one another. Tertiary structure is generally stabilized by nonlocal interactions, most commonly the formation of a hydrophobic core, but also through salt bridges, hydrogen bonds, disulfide bonds, and even posttranslational modifications. The term "tertiary structure" is often used as synonymous with the term fold. The tertiary structure is what controls the basic function of the protein.

*Quaternary structure*: the structure formed by several protein molecules (polypeptide chains), usually called protein subunits in this context, which function as a single protein complex.

Proteins can be informally divided into three main classes: *fibrous proteins*, *globular proteins* and *membrane proteins*.

***Fibrous (structural) proteins.*** As the name implies, these substances have fiber-like structures, and serve as the chief structural material in various tissues. Corresponding to this structural function, they are relatively insoluble in water and unaffected by moderate changes in temperature and pH. Subgroups within this category include: Collagens and Elastins, the proteins of connective tissues, tendons and ligaments; Keratins, proteins that are major components of skin, hair, feathers and horn; Fibrin, a protein formed when blood clots.

**Globular Proteins.** Members of this class serve regulatory, maintenance and catalytic roles in living organisms. They include hormones, antibodies and enzymes and either dissolve or form colloidal suspensions in water. Such proteins are generally more sensitive to temperature and pH change than their fibrous counterparts.

**Membrane proteins.** They often serve as receptors or provide channels for polar or charged molecules to pass through the cell membrane.

### Physicochemical properties of proteins

**The molecular weight.** Proteins cannot be determined by the methods of classical chemistry (e. g., freezing-point depression), because they require solutions of a higher concentration of protein than can be prepared.

The method most frequently used to determine the molecular weight of proteins is ultracentrifugation – i. e., spinning in a centrifuge at velocities up to about 60,000 revolutions per minute. Centrifugal forces of more than 200,000 times the gravitational force on the surface of Earth are achieved at such velocities. The first ultracentrifuges, built in 1920, were used to determine the molecular weight of proteins. The molecular weights of a large number of proteins have been determined.

**The shape of protein molecules.** In the technique of X-ray diffraction, the X-rays are allowed to strike a protein crystal. The X-rays, diffracted (bent) by the crystal, impinge on a photographic plate, forming a pattern of spots. This method reveals that peptide chains can assume very complicated, apparently irregular shapes. Two extremes in shape include the closely folded structure of the globular proteins and the elongated, unidimensional structure of the threadlike fibrous proteins. Solutions of fibrous proteins are extremely viscous (i. e., sticky); those of the globular proteins have low viscosity (i. e., they flow easily).

**Hydration of proteins.** In aqueous solutions, proteins bind some of the water molecules very firmly; others are either very loosely bound or form islands of water molecules between loops of folded peptide chains. Because the water molecules in such an island are thought to be oriented as in ice, which is crystalline water, the islands of water in proteins are called icebergs. Hydration of proteins is necessary for their solubility in water. If the water of hydration of a protein dissolved in water is reduced by the addition of a salt such as ammonium sulfate, the protein is no longer soluble and is salted out, or precipitated. The salting-out process is reversible because the protein is not denatured

(i. e., irreversibly converted to an insoluble material) by the addition of such salts as sodium chloride, sodium sulfate, or ammonium sulfate. Some globulins, called euglobulins, are insoluble in water in the absence of salts.

**Protein denaturation.** When a solution of a protein is boiled, the protein frequently becomes insoluble – i. e., it is denatured – and remains insoluble even when the solution is cooled. The denaturation of the proteins of egg white by heat – as when boiling an egg – is an example of irreversible denaturation. The denatured protein has the same primary structure as the original, or native, protein. In some instances the original structure of the protein can be regenerated; the process is called renaturation. Denaturation can be brought about in various ways. Proteins are denatured by treatment with alkaline or acid, oxidizing or reducing agents, and certain organic solvents. The agents most frequently used for this purpose are urea and guanidinium chloride.

### Classification by biological functions

It is preferable to classify the proteins according to their biological function. Such a classification is far from ideal, however, because one protein can have more than one function. Another problem with functional classification is that the definite function of a protein frequently is not known.

The number of existing proteins is immense. We would like to mention only some of them.

**Structural (fibrous) proteins.** Scleroprotein, any of several fibrous proteins of cells and tissues once thought to be insoluble but now known to be dissolved by dilute solutions of acids such as citric and acetic. The two most important classes of scleroproteins are the collagens and the keratins.

**The muscle proteins.** The total amount of muscle proteins in mammals, including man, exceeds that of any other protein. Thus, the human body contains about five to six kilograms (11 to 13 pounds) of muscle protein. In contrast to the scleroproteins, the contractile proteins are soluble in salt solutions and susceptible to enzymatic digestion.

**Fibrinogen,** the protein of the blood plasma, is converted into the insoluble protein fibrin during the clotting process. The fibrinogen-free fluid obtained after removal of the clot, called blood serum, is blood plasma minus fibrinogen.

*Collagen* is the structural protein of bones, tendons, ligaments, and skin. For many years collagen was considered to be insoluble in water.

*Keratin* is the structural protein of epithelial cells in the outermost layers of the skin. It has been isolated from hair, nails, hoofs, and feathers. Keratin is completely insoluble in cold or hot water.

*Milk proteins.* Milk contains the following: an albumin,  $\alpha$ -lactalbumin; a globulin, beta-lactoglobulin; and a phosphoprotein, casein. If acid is added to milk, casein precipitates.

*Egg proteins.* About 50 percent of the proteins of egg white are composed of ovalbumin, which is easily obtained in crystals. Its molecular weight is 46,000 and its amino acid composition differs from that of serum albumin. Other proteins of egg white are conalbumin, lysozyme, ovoglobulin, ovomucoid, and avidin.

*Hemoglobin* is an iron-containing protein in the blood of many animals – in the red blood cells (erythrocytes) of vertebrates – that transports oxygen to the tissues.

Proteins are considered to be macromolecular polypeptides – i. e., very large molecules composed of many peptide-bonded amino acids. Most of the common ones contain more than 100 amino acids linked to each other in a long peptide chain.

*Peptide* is any organic substance of which the molecules are structurally like those of proteins, but smaller. The class of peptides includes many hormones, antibiotics, and other compounds that participate in the metabolic functions of living organisms. Peptide molecules are composed of two or more amino acids joined through amide formation involving the carboxyl group of each amino acid and the amino group of the next. The chemical bond between the carbon and nitrogen atoms of each amide group is called a *peptide bond*. Some or all of the peptide bonds, which connect the consecutive triplets of atoms in the chain regarded as the backbone of the molecule, can be broken by partial or complete hydrolysis of the compound. This reaction, producing smaller peptides and finally the individual amino acids, is commonly used in studies of the composition and structure of peptides and proteins.

The number of amino-acid molecules present in a peptide is indicated by a prefix: a dipeptide contains two amino acids; an octapeptide, eight; an oligopeptide, a few; a polypeptide, many.

Peptides are distinguished from proteins on the basis of size, and as an arbitrary benchmark can be understood to contain approximately 50 or fewer amino acids. Proteins consist of one or more polypeptides arranged in a biologically functional way, often bound to ligands such

as coenzymes and cofactors, or to another protein or other macromolecule (DNA, RNA, etc.), or to complex macromolecular assemblies. Finally, while aspects of the lab techniques applied to peptides versus polypeptides and proteins differ (e. g., the specifics of electrophoresis, chromatography, etc.), the size boundaries that distinguish peptides from polypeptides and proteins are not absolute. Long peptides such as amyloid beta have been referred to as proteins, and smaller proteins like insulin have been considered peptides.

### REVISION EXERCISES

#### **Ex. 1. Answer the following questions.**

1. What is protein? What does the Greek word “proteios” mean?
2. How many amino acids occur naturally in proteins? 3. Can animals and humans synthesize all of the amino acids essential for life? What must they obtain proteins from? 4. What do enzymes allow the organism to do? 5. What organic substances perform important regulatory functions in human’s organism? 6. What do biochemists often refer to? 7. How many classes can proteins be informally divided into? 8. What are the most important physicochemical properties of proteins? 9. What classification of proteins is today widely used? 10. What are peptides?

#### **Ex. 2. Match the words with their definitions.**

- |                      |   |
|----------------------|---|
| 1) organ-specific    | a) the change of folding structure of a protein (thus of physical properties) caused by heating, changes in pH, or exposure to certain chemicals  |
| 2) species-specific  | b) produced by the injection of the cells of a certain organ or tissue  |
| 3) liver             | c) a number of things arranged in a line or row   |
| 4) string, alignment | d) the largest glandular organ in vertebrate animals, located in the upper or anterior part of the abdomen: it secretes bile, has an important function in the storage and metabolism of carbohydrates, fats, and proteins, and helps detoxify many poisonous substances that may be ingested |
| 5) provide           | e) to let go, to set free   |
| 6) legume            | f) limited to or found only in one species  |
| 7) denaturation      | g) the pod or seed of some members of this order, used for food   |
| 8) release           | h) to supply or make available  |

**Ex. 3. Say whether the following statements are true or false.**

1. Proteins of similar function differ greatly in amino acid composition and sequence. 2. Protein molecules are produced in cells and are allowed to be put into circulation within the organism only after synthesis is complete. 3. Enzymes are crucial for accomplishing all metabolic reactions. 4. The tertiary structure controls the basic function of the protein. 5. Fibrous (structural) proteins serve regulatory, maintenance and catalytic roles in living organisms. 6. Ultracentrifugation is often used to determine the molecular weight of proteins. 7. A prefix shows how many amino-acid molecules present in a peptide.

**Ex. 4. Insert the necessary word.**

1. Hemoglobin is ... in the blood of many animals and humans that ... oxygen to the tissues. 2. Hemoglobin forms an unstable, ... with oxygen. 3. In the oxygenated state it is called oxyhemoglobin and is ...; in the reduced state it is ... . 4. Each hemoglobin molecule is ... of four heme groups surrounding a globin group, forming a tetrahedral structure. 5. There are four iron atoms in each molecule of hemoglobin, which accordingly can ... four atoms of oxygen.

made up, an iron-containing protein, bright red, transports, bind, purplish blue, reversible bond
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# UNIT XVIII

## CATALYSTS AND REACTION CONDITIONS

A chemical reaction involves a chemical change, which happens when two or more particles (which can be molecules, atoms or ions) interact. For example, when iron and oxygen react, they change to a new substance, iron oxide (rust). Iron oxide has different chemical properties to iron and oxygen. This is different to a physical change. For example, water can turn to ice, but ice is still water in another physical state – ice and water have the same chemical properties.

When chemicals react, particles need to collide with each with enough energy for a reaction to take place. The more often they collide, the more likely they are to react. Not all collisions result in reactions – often there is not enough energy for this to happen.

Some reactions happen faster than others. The rate depends on the likelihood of collision between particles. A number of things affect the rate of a reaction.

**Concentration.** The more particles there are, the bigger the chance of collisions.

**Temperature.** Particles move around more at higher temperatures, so more collisions are likely, and the collisions will have more energy.

**Pressure.** Particles in gases are very spread out. If you increase the pressure, the particles are forced together, so the chances of collision are increased.

**Surface area.** If one of the reacting chemicals is a solid, only particles at the surface can collide. The bigger the surface, the faster the reaction. Smaller particles have a larger surface area for their size than larger ones. This explains why powder normally reacts faster than lumps.

**Catalysts.** A catalyst is a substance that changes the rate of a chemical reaction, but is chemically unchanged at the end of the reaction. An inhibitor does the opposite – it slows down chemical reaction.

Catalysts play an important part in many chemical processes. They increase the rate of reaction, are not consumed by the reaction and are only needed in very small amounts. There are two main ways that catalysts work.

**Adsorption.** Particles stick onto the surface of the catalyst (called adsorption) and then move around, so they are more likely to collide and react. A good example is the way the platinum catalyst in a car's

catalytic converter works to change toxic carbon monoxide into less-toxic carbon dioxide.

**Intermediate compounds.** In this process, a catalyst first combines with a chemical to make a new compound. This new compound is unstable, so it breaks down, releasing another new compound and leaving the catalyst in its original form. Many enzymes (special biological catalysts) work in this way. Many industrial chemical processes rely on such catalysts.

One example of a catalyst that involves an intermediate compound can be found high in the Earth's atmosphere. Up there, the chemical ozone (with molecules containing three oxygen atoms) helps protect the Earth from harmful UV radiation. But also up there is chlorine, which gets into the atmosphere from chemicals (chlorofluorocarbons, CFCs) used in some refrigerators, air conditioners and aerosol cans.

Chlorine is a catalyst, which steals an oxygen atom from ozone ( $O_3$ ) leaving stable oxygen ( $O_2$ ). At the same time, it forms an unstable intermediate chlorine-oxygen compound, which breaks down to release its oxygen. This leaves the chlorine free to repeat the process. One chlorine atom can destroy about a million ozone molecules every second. This can have a drastic effect on the atmosphere's ability to protect us from UV radiation.

## Enzymes

Enzymes are biological catalysts. They are proteins that fold into particular conformations such that they can help speed up very particular chemical reactions. For biochemical reactions, the reactant is typically called the substrate. The substrate is converted into the product. The mechanisms for many enzymes are very similar. The substrate(s) and the enzyme bind into a complex. The physical location on the enzyme in which the substrate binds is called the "active site". Once bound, this complex can then weaken particular bonds in the substrate such that chemistry occurs to form the product. The product is weakly bound to the substrate such that it now dissociates and the enzyme is free to bind another substrate molecule.

The active sites in enzymes can be very specific such that the enzyme will only catalyze a very specific reaction for a very specific molecule. Typically there is equilibrium between the bound complex and the free substrate and enzyme such that the binding could be reversible. In contrast, once the product is formed the backward reaction typically will never happen:



The activity of many enzymes can be blocked by molecules which mimic the substrate but don't do any chemistry. These molecules then effectively "turn off" the enzyme by blocking the active site and preventing binding of the substrate. Many pharmaceutical drugs operate in this way. Such molecules are typically called inhibitors as they inhibit the activity of the enzyme.

Enzymes are naturally occurring catalysts responsible for many essential biochemical reactions. Most solid catalysts are metals or the oxides, sulfides, and halides of metallic elements and of the semi-metallic elements boron, aluminum, and silicon. Gaseous and liquid catalysts are commonly used in their pure form or in combination with suitable carriers or solvents; solid catalysts are commonly dispersed in other substances known as catalyst supports.

In general, catalytic action is a chemical reaction between the catalyst and a reactant, forming chemical intermediates that are able to react more readily with each other or with another reactant, to form the desired end product. During the reaction between the chemical intermediates and the reactants, the catalyst is regenerated. The modes of reactions between the catalysts and the reactants vary widely and in solid catalysts are often complex. Typical of these reactions are acid-base reactions, oxidation-reduction reactions, formation of coordination complexes, and formation of free radicals. With solid catalysts the reaction mechanism is strongly influenced by surface properties and electronic or crystal structures. Certain solid catalysts, called polyfunctional catalysts, are capable of more than one mode of interaction with the reactants; bifunctional catalysts are used extensively for reforming reactions in the petroleum industry.

Catalyzed reactions form the basis of many industrial chemical processes. Catalyst manufacture is itself a rapidly growing industrial process.

## REVISION EXERCISES

### Ex. 1. Answer the following questions.

1. What are physical and chemical changes?
2. How does a chemical reaction proceed?
3. What factors affect the rate of a reaction?
4. What is the definition of a catalyst?
5. What way do catalysts work

in? 6. How does chlorine work as catalyst? 7. What are inhibitors?  
8. What are enzymes? 9. Can enzymes be blocked?

**Ex. 2. Match the words with their definitions.**

- |               |  |
|---------------|--|
| 1) collision  | a) any of numerous complex proteins that are produced by living cells and catalyze specific biochemical reactions at body temperatures |
| 2) drastic    | b) capable of going through a series of actions (as changes) either backward or forward  |
| 3) likelihood | c) to allow (a substance) to enter the air, water, soil, etc.; to set free from restraint  |
| 4) release    | d) to use (fuel, time, resources, etc.)  |
| 5) consume    | e) the chance that something will happen   |
| 6) enzyme     | f) an encounter between particles (as atoms or molecules) resulting in exchange or transformation of energy                            |
| 7) reversible | g) extreme in effect or action: severe or serious  |

**Ex. 3. Say whether the following statements are true or false.**

1. When chemicals react, particles need to collide with each with enough energy for a reaction to take place. 2. Catalysts in the same phase are called homogeneous catalysts, while those in different phases are called heterogeneous catalysts. 3. A catalyst is a substance that slows down the rate of a chemical reaction but is not consumed during the course of the reaction. 4. Many reactions are catalyzed inside metals. 5. The catalysts speed up all reactions. 6. With solid catalysts the reaction mechanism is strongly influenced by surface properties and electronic or crystal structures. 7. Enzymes are artificial catalysts responsible for many essential biochemical reactions.

**Ex. 4. Insert the necessary word.**

1. A catalyst is a chemical substance that ... the rate of a chemical reaction by altering the activation energy required for the reaction to proceed. 2. This is called catalysis. 3. A catalyst is not consumed by the reaction and it may ... in multiple reactions at a time. 4. The only difference between a catalyzed reaction and an uncatalyzed reaction is that the ... energy is different. 5. There is no effect on the energy of the reactants or the products. 6. Positive and negative catalysts: usually when someone refers to a catalyst, they mean a positive catalyst, which is a catalyst which ... the rate of a chemical reaction by lowering its activation energy. 7. There are also negative catalysts or inhibitors, which ... the rate of a chemical reaction or make it less likely to occur.

8. Promoters and catalytic poisons: a promoter is a substance that ... the activity of catalyst. 9. A catalytic poison is a substance that inactivates a catalyst.

slow, participate, increases, affect, speeds up, activation

**Ex. 5. Translate the following text.**

**Catalyst.** A catalyst is a substance that speeds up the rate of a chemical reaction but is not consumed during the course of the reaction. A catalyst will appear in the steps of a reaction mechanism, but it will not appear in the overall chemical reaction (as it is not a reactant or product). Generally, catalysts alter the mechanism of the reaction in a substantial way such that the new barriers along the reaction coordinate are significantly lower. By lowering the activation energy, the rate constant is greatly increased (at the same temperature) relative to the uncatalyzed reaction.

There are many types of catalysts in the world. Many reactions are catalyzed at the surface of metals. In biochemistry, enormous numbers of reactions are catalyzed by enzymes. Catalysts can either be in the same phase as the chemical reactants or in a distinct phase.

Catalysts in the same phase are called *homogeneous catalysts*, while those in different phases are called *heterogeneous catalysts*. For example, if we have Pt metal as a catalyst for the reaction of hydrogen gas and ethene gas, then the Pt is a heterogeneous catalyst. However, an enzyme in solution catalyzing a solution phase biochemical reaction is a homogeneous catalyst.

Another important idea about catalysts is that they are selective. That is the catalyst doesn't just speed up all reactions, but only a very particular reaction. This is the key to many chemical transformations. When you only want to perform a particular chemical change, you look for a catalyst that will speed up that specific reaction but not others. Enzymes are remarkable in this way. Living biological systems require a myriad of specific chemical transformations and there is a unique enzyme to catalyze each of them.

**Effect of catalysts.** The effect of a catalyst is that it lowers the activation energy for a reaction. Generally, this happens because the catalyst changes the way the reaction happens (the mechanism). We can visualize this for a simple reaction coordinate in the following way. In a more generally sense, the catalyzed reaction may have a number of new barriers and intermediates. However, the highest barrier will now be significantly lower than the previous largest barrier.

# UNIT XIX

## BIOACTIVE COMPOUNDS AND BIOCHEMISTRY

A *bioactive compound* is a compound that has an effect on a living organism, tissue or cell. In the field of nutrition bioactive compounds are distinguished from essential nutrients. While nutrients are essential to the sustainability of a body, the bioactive compounds are not essential since the body can function properly without them, or because nutrients fulfil the same function. Bioactive compounds can have an influence on health.

Bioactive compounds are found in both plant and animal products or can be synthetically produced. Examples of plant bioactive compounds are carotenoids and polyphenols (from fruits and vegetables), or phytosterols (from oils). Example in animal products are fatty acids, found in milk and fish. Some examples of bioactive compounds are flavonoids, caffeine, carotenoids, carnitine, choline, coenzyme Q, creatine, phytosterols, polysaccharides, glucosinolates, polyphenols, anthocyanins prebiotics, taurine and others.

There are two biggest classes of bioactive compounds. They are hormones and vitamins.

### Hormones

Hormones are organic substances secreted by plants and animals. They are special chemical messengers in the body that are created in the endocrine glands. These messengers control most major bodily functions, e. g. such as digestion, metabolism, respiration, tissue function, sensory perception, sleep, excretion, lactation, stress, growth and development, movement, reproduction, and even mood.

Hormones affect distant cells by binding to specific receptor proteins in the target cell resulting in a change in cell function.

Hormone synthesis may occur in specific tissues of endocrine glands or in other specialized cells, which are part of the endocrine system. Hormone synthesis occurs in response to specific biochemical signals induced by a wide range of regulatory systems. The main hormone-producing glands are: *hypothalamus* being responsible for body temperature, hunger, moods and the release of hormones from other glands and controlling thirst, sleep and sex drive; *parathyroid* controlling

the amount of calcium in the body; *thymus*, playing a role in the function of the adaptive immune system and the maturity of the thymus and producing T-cells; *pancreas* producing the insulin that helps control blood sugar levels; *thyroid* producing hormones associated with calorie burning and heart rate; *adrenal* producing the hormones that control sex drive and cortisol, the stress hormone; *pituitary* controlling other glands; *pineal*, also called the thalamus, producing serotonin derivatives of melatonin, which affects sleep; *ovaries*, only in women, secreting estrogen, testosterone and progesterone, the female sex hormones; *testes*, only in men, producing the male sex hormone, testosterone, and produce sperm. These glands work together to create and manage the body's major hormones.

Hormones have diverse chemical structures, mainly of 3 classes: eicosanoids, steroids, and amino acid derivatives (amines, peptides, and proteins).

### Major types of hormones

The body has many different hormones, but certain types have a bigger role to play in the body's health and well-being. Understanding these roles is important for those looking to protect and manage their health. We would like to mention some of them:

*Cortisol* has been called the “stress hormone” because of the way it assists the body in responding to stress. This is just one of several functions of this important hormone.

*Adrenaline* triggers the body's fight-or-flight response. This reaction causes air passages to dilate to provide the muscles with the oxygen they need to either fight danger or flee. Adrenaline also triggers the blood vessels to contract to re-direct blood toward major muscle groups, including the heart and lungs. The body's ability to feel pain also decreases as a result of adrenaline, which is why you can continue running from or fighting danger even when injured. Adrenaline causes a noticeable increase in strength and performance, as well as heightened awareness, in stressful times. After the stress has subsided, adrenaline's effect can last for up to an hour.

*Thyroxine* plays a crucial role in heart and digestive function, metabolism, brain development, bone health and muscle control. It affects almost all of the body's systems, which means proper thyroxine levels are vital for health.

*Melatonin* (“sleep hormone”) is essential to signaling the relaxation and lower body temperature that help with restful sleep. Levels of melatonin are higher at night, signaling the body that it is time to rest. Melatonin levels change throughout the day

*Insulin* allows the cells in the muscles, fat and liver to absorb glucose that is in the blood. Insulin production and release is a tightly regulated process, allowing the body to balance its metabolic needs.

## Vitamins

The value of eating a certain food to maintain health was recognized long before vitamins were identified. The ancient Egyptians knew that feeding liver to a person would help cure night blindness, an illness now known to be caused by a vitamin A deficiency. The advancement of ocean voyages during the Renaissance resulted in prolonged periods without access to fresh fruits and vegetables, and made illnesses from vitamin deficiency common among ships’ crews. In 1747, the Scottish surgeon James Lind discovered that citrus foods helped prevent scurvy, a particularly deadly disease in which collagen is not properly formed, causing poor wound healing, bleeding of the gums, severe pain, and death. The term “vitamine” appeared in 1912. It consisted of two words “vital” and “amine”. However, in 1920, it was determined that newly discovered vitamin C did not contain amine component and the letter “e” was removed from the name.

Vitamins may be defined as organic substances that play a required catalytic role within the cell (usually as components of coenzymes or other groups associated with enzymes) and must be obtained in limited amounts through the diet. Vitamin requirements are specific for each organism, and their deficiency may cause disease.

Vitamins are classified as either *water-soluble* or *fat-soluble*. In humans there are 13 vitamins: 4 fat-soluble (A, D, E, and K) and 9 water-soluble (8 vitamins B and vitamin C). Many types of water-soluble vitamins are synthesized by bacteria. Fat-soluble vitamins are absorbed through the intestinal tract with the help of lipids (fats). Because they are more likely to accumulate in the body, they are more likely to lead to hypervitaminosis than are water-soluble vitamins. Fat-soluble vitamin regulation is of particular significance in cystic fibrosis.

Although a vitamin is usually defined as an organic chemical which an animal or human must obtain from the diet, this is not entirely true. There are some examples.

*Vitamin A* does not occur in the plant kingdom, but the pigment carotene is universally present in green plants, and most animals can split a molecule of carotene into two molecules of vitamin A. The exceptions are cats and probably other carnivores, which under natural conditions have to obtain the preformed vitamin by consuming the tissues of other animals. Niacin, too, is not an absolute requirement, since most animals (cats again being an exception) can synthesize it from the amino acid tryptophan if the latter is present in excess of its use for protein synthesis.

*Vitamin D* is not a true vitamin: most species do not need it in their diet, because they obtain an adequate supply through the exposure of skin to sunlight, which converts a sterol present in dermal tissue to vitamin D. The vitamin is subsequently metabolized to form a hormone that acts to control the absorption and utilization of calcium and phosphate. Animals such as rodents, which normally have little exposure to sunlight and search for food mostly at night, appear to have evolved so as to be independent of vitamin D so long as their intakes of calcium and phosphate are well-balanced.

*Vitamin C* (ascorbic acid) is an essential chemical in the tissues of all species, but most can make it for themselves, so that for them it is not a vitamin. Presumably, species that cannot synthesize vitamin C – they include humans, guinea pigs, and fruit-eating bats – had ancestors that lost the ability at a time when their diet was rich in ascorbic acid.

Bacteria vary greatly in their need for vitamins. Many are entirely independent of outside sources, but at the other extreme some of the strains of bacteria found in milk (i. e., *Lactobacillus*) have lost the ability to synthesize the *B vitamins* that they need. This property has made them useful for assaying extracts of foods for their vitamin B content. Indeed, many vitamins of this group were first discovered as growth factors for bacteria before being tested with animals and humans. The mixed bacterial flora in the guts of animals are, on balance, synthesizers of the B vitamins.

For one B vitamin – cobalamin, or vitamin B12 – bacterial fermentation is the only source, though it can be obtained indirectly from the tissues or milk of animals that have obtained it themselves from bacteria. The generalization that “the animal kingdom lives on the plant kingdom” is therefore not the whole truth, because animals rely partly on bacteria for this one micronutrient.

Sellers of bioactive substances often attribute health benefits to these compounds, but there is insufficient research into the effectiveness

and safety of these substances, either in long term use or in quantities that exceed normal consumption levels. In addition, some flavonoids have been shown to influence the effects of drugs. However, a number of bioactive substances have been shown to act as antioxidants. As bioactive compounds are not essential, advice on daily intake is often unregulated.

## **Biochemistry**

Biochemistry is the branch of science that explores the chemical processes within and related to living organisms. It is a laboratory based science that brings together biology and chemistry. By using chemical knowledge and techniques, biochemists can understand and solve biological problems.

Biochemistry focuses on processes happening at a molecular level. It focuses on what's happening inside our cells, studying components like proteins, lipids and organelles. It also looks at how cells communicate with each other, for example during growth or fighting illness. Biochemists need to understand how the structure of a molecule relates to its function, allowing them to predict how molecules will interact.

Biochemistry covers a range of scientific disciplines, including genetics, microbiology, forensics, plant science and medicine. Because of its breadth, biochemistry is very important and advances in this field of science over the past 100 years have been staggering. It's a very exciting time to be part of this fascinating area of study.

Biochemists:

- provide new ideas and experiments to understand how life works;
- support our understanding of health and disease;
- contribute innovative information to the technology revolution;
- work alongside chemists, physicists, healthcare professionals, policy makers, engineers and many more professionals.

## **Methods in biochemistry**

Like other sciences, biochemistry aims at quantifying, or measuring, results, sometimes with sophisticated instrumentation. The earliest approach to a study of the events in a living organism was an analysis of the materials entering an organism (foods, oxygen) and those leaving (excretion products, carbon dioxide). This is still the basis of so-called balance experiments conducted on animals, in which, for example, both foods and excreta are thoroughly analyzed. For this purpose many

chemical methods involving specific colour reactions have been developed, requiring spectrum-analyzing instruments (spectrophotometers) for quantitative measurement. Gasometric techniques are those commonly used for measurements of oxygen and carbon dioxide, yielding respiratory quotients (the ratio of carbon dioxide to oxygen). Somewhat more detail has been gained by determining the quantities of substances entering and leaving a given organ and also by incubating slices of a tissue in a physiological medium outside the body and analyzing the changes that occur in the medium. Because these techniques yield an overall picture of metabolic capacities, it became necessary to disrupt cellular structure (homogenization) and to isolate the individual parts of the cell – nuclei, mitochondria, lysosomes, ribosomes, membranes – and finally the various enzymes and discrete chemical substances of the cell in an attempt to understand the chemistry of life more fully.

### REVISION EXERCISES

#### **Ex. 1. Answer the following questions.**

1. What is a bioactive compound? 2. Where bioactive compounds can be found? 3. What are the biggest classes of bioactive compounds? 4. Where may hormone synthesis occur in? 5. What are the main hormone-producing glands? 6. How can vitamins be classified? 7. Do bioactive substances benefit human health? 8. What is biochemistry? 9. What are the main purposes of biochemistry? 10. What are the most widely used methods of biochemistry?

#### **Ex. 2. Match the words with their definitions.**

- |                  |  |
|------------------|--|
| 1) tissue        | a) substance that prevents or repairs the process of oxidation                         |
| 2) trigger       | b) to produce or give something to another   |
| 3) antioxidant   | c) something that is essential or vitally important                                    |
| 4) crucial       | d) to engage in verbal or physical contact with someone else                           |
| 5) consumption   | e) to fire a gun or to start a series of events or emotions                            |
| 6) interact      | f) someone that is intelligently worldly and smart or advanced processes or technology |
| 7) sophisticated | g) buying and using something or how much of something has been used up                |
| 8) yield         | h) group of cells, or an absorbent paper, or thin paper used for wrapping gifts        |

**Ex. 3. Say whether the following statements are true or false.**

1. Bioactive compounds cannot be synthesized; they should be obtained from the diet. 2. Bioactive compounds are important just for the metabolic processes; they don't have an influence on health. 3. Hormones control main functions of the body, even your mood depend on them. 4. The endocrine glands of the organism operate as one team. 5. Vitamin requirements are general for all people. 6. The more vitamins people take, the better it is for their health. 7. By using chemical knowledge and techniques, biochemists can understand and solve different problems of inorganic chemistry.

**Ex. 4. Insert the necessary word.**

1. Biochemistry is the study of the chemistry of ... . 2. It is a vast and exciting field in which important discoveries about how life is maintained and how ... occur are being made every day. 3. In particular, there has been rapid growth in the understanding of how living cells manufacture and ... necessary for life. 4. This not only has been beneficial for detection and ... but also has spawned a new field – ..., which uses nature's "machinery" to synthesize desired substances. 5. Many other products, including ..., are also being produced by the techniques of biotechnology. 6. An understanding of biochemistry also allows our society to produce ... .

treatment of diseases, healthier processed foods, living systems, use the molecules, biotechnology, diseases, natural pesticides
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# HOW TO READ CHEMICAL REACTIONS

+ is read: plus, and, together with, react with;

– is not read (it designates one bond);

= is read: give, form, produce;

→ is read: give, pass over, lead to;

↔ is read: forms and is formed from;

$C + O_2 \rightarrow CO_2$  is read: C plus O two give CO two or one atom of carbon reacts with one two-atom molecule of oxygen and produces one molecule of carbon dioxide;

$2H_2 + O_2 \rightarrow 2H_2O$  is read: two molecules of H two plus O two give two molecules of H two O. Another variant: two atom-molecules of hydrogen react with one two-atom molecule of oxygen and produce two molecules of water;

$N_2 + 3H_2 \leftrightarrow 2NH_3$  is read: N two plus three molecules of H two form and are formed from two molecules of NH three.

Reading of an equation:  $Zn + H_2SO_4 \leftrightarrow ZnSO_4 + H_2$ .

The “plus” sign on the left of the arrow means “reacts with”; the arrow means “forming” or “producing”; and the “plus” sign on the right of the arrow means “and”.

So this equation is read: “One atom of zinc reacts with one molecule of sulphuric acid producing one molecule of zinc sulphate and one molecule of hydrogen.”

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