

1. General Chemistry

1.1 Fundamentals of Chemistry

Chemistry is concerned with the properties of chemicals and with the changes chemicals can undergo. **Chemicals** are any substances that have a definite composition.

Chemical reaction is the process by which one or more substances change to produce one or more different substances. In a chemical change, the identities of substances change and new substances form.

Reactant is a substance or molecule that participates in a chemical reaction.

Product is a substance that forms in a chemical reaction.

Intensive properties, like temperature, have values that do not depend on the amount of sample.

Extensive properties, like length and volume, have values that *do* depend on the sample size.

Physical properties are characteristics; they do not involve a change in a sample's chemical makeup.

Chemical properties are characteristics that *do* involve a change in chemical makeup.

The law of conservation of mass states that the mass of the reactants in a reaction equals the mass of the products.

Atom: all matter is composed of extremely small particles called atoms. Atoms of a given **element** (it is a substance from the same atoms) are identical in their physical and chemical properties. Atoms of different elements differ in their physical and chemical properties. Each element is characterized by the mass of its atoms. Atoms of the same element have the same mass, but atoms of different elements have different masses. According to the **law of multiple proportions**, atoms of different elements combine in simple, whole-number ratios to form compounds. **Compounds** are pure material formed from the atoms of two or more elements and their physical or chemical properties are not directly related to any of their components.

1.2. Structure of Atoms

Atoms can be broken into pieces and these smaller parts that make up atoms are called **subatomic particles**. The three particles that are most important for chemistry are **electrons**, **protons** and **neutrons**.

Electron is a part of atoms of all elements that has mass and a negative charge.

Protons and neutrons compose the **nucleus**. The nucleus has all of the positive charge, nearly all of the mass, but only a very small fraction of the volume of the atom.

Neutron is a subatomic particle that has no charge.

Proton is a subatomic particle that has a positive charge. Elements differ from each other in the number of protons their atoms contain. The number of protons that an atom has is known as the atom's atomic number. **Atomic number** the number of protons in the nucleus of an atom; the atomic number is the same for all atoms of an element.

All atoms consist of protons and electrons. Most atoms also have neutrons. Protons and neutrons make up the small, dense nuclei of atoms. The electrons occupy the space surrounding the nucleus.

Every atomic nucleus can be described not only by its atomic number but also by its mass number. The **mass number (A)** is equal to the total number of particles of the nucleus, that is, the total number of protons (Z) and neutrons (N). That is, **A=Z+N**.

All atoms of an element have the same atomic number, because of the same number of protons. Atoms of the same element that have different numbers of neutrons are called **isotopes**. All isotopes of an element have the same atomic number. Their atomic masses are not the same because the number of neutrons of the atomic nucleus of each isotope varies.

Radioactivity is the spontaneous breakdown of unstable nuclei to produce particles or energy.

For the current best interpretation of atomic structure, the **quantum mechanics model** helps. The basic idea of the model uses that every particle has wavelengths, so the movement of electrons coincides with the wave propagation. The phenomena associated with electrons in the atoms can therefore be discussed in the same way as functions describing wave motion. The most likely spatial location of the electron can be given in around of the nucleus. Electrons with different energies may be characterized by different resident probabilities. These are considered to be the "paths" of electrons, they are called **electron orbitals**.

All the electrons in the atom can be described by **four quantum numbers** (n , l , m_l and m_s) that determine the electron's energy and spatial position. Quantum numbers represented that describe the orbital energy level and the three-dimensional shape of the region occupied by electrons in a given space.

The principal quantum number (n) is a positive integer ($n= 1,2,3...7$) on which the size and energy level of the orbital primarily depend. If the electron is further away from the nucleus, then n is higher, the energy of the electron is greater.

The angular-momentum quantum number (l) defines the three-dimensional shape of the orbital. For an orbital whose principal quantum number is n , the angular-momentum quantum number l can have any integral value **from 0 to $n-1$** .

According to the principal quantum number n , orbitals as being grouped into **shells**, and orbitals as being grouped into **subshells** according to the angular-momentum quantum number l . Different subshells are usually referred to by letter rather than by number, following the order s , p , d , f . When the quantum number l : 0, 1, 2 or 3, the subshell notation: s , p , d , f .

The **magnetic quantum number** (m_l) defines the spatial orientation of the orbital. For an orbital whose angular-momentum quantum number is l , the magnetic quantum number m_l can have any integral value from $-l$ to $+l$. Thus, within each subshell (orbitals with the same shape, or value of l), there are different spatial orientations for those orbitals.

Electrons are free to spin in either a clockwise or a counter clockwise direction. This spinning charge gives rise to a tiny magnetic field and to a **spin quantum number (m_s)**, which can have either of two values, $+1/2$ or $-1/2$.

Knowing the relative energies of the various orbitals, we can predict for each element which orbitals are occupied by electrons, the element's **electron configuration**. A set of three rules called the **aufbau principle** (from the German word for "building up") guides the filling order of orbitals. In general, each successive electron added to an atom occupies the lowest-energy orbital available. The resultant **lowest-energy electron configuration** is called the **ground-state configuration** of the atom.

Rules of the aufbau principle:

1. Lower-energy orbitals fill before higher-energy orbitals.
2. An orbital can hold only two electrons, which must have opposite spins. This is just a restatement of the **Pauli's exclusion principle**: no two electrons in an atom can have the same four quantum numbers.
3. If two or more degenerate orbitals are available, one electron goes into each until all are half-full, a statement called **Hund's rule**. Only then does a second electron fill one of the

orbitals. Furthermore, the electrons in each of the singly occupied orbitals must have the same value for their spin quantum number.

The periodic system of the elements:

Periodic law is the law that states that the repeating physical and chemical properties of elements change periodically with their atomic number. The modern periodic system is based on the order of energy levels of the subshell: $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s \rightarrow 4f \rightarrow 5d \rightarrow 6p \rightarrow 7s \rightarrow 5f \rightarrow 6d \rightarrow 7p$

Elements in each column of the table have the same number of electrons in their outer energy level. These electrons are called valence electrons.

Valence electron is an electron that is found in the outermost shell of an atom and that determines the atom's chemical properties. **Group** is a vertical column of elements in the **periodic table**; elements in a group share chemical properties.

A horizontal row on the periodic table is called a **period**. Elements in the same period have the same number of occupied energy levels.

Blocks of the periodic table, are corresponding to filling the different kinds of orbitals. Beginning at the top left and going across successive rows of the periodic table provides a method for remembering the order of orbital filling.

Classification of the elements

Focusing only on the electrons in the outermost shell, called the **valence shell**. All the elements in a given group of the periodic table have similar valence-shell electron configurations. The **periodic table** can be divided into four regions, or blocks, of elements according to the orbitals being filled. The group 1A and 2A elements on the left side of the table are called the **s-block elements**, because they result from the filling of an s orbital; the group 3A–8A elements on the right side of the table are the **p-block elements**, because they result from the filling of p orbitals; the transition metal **d-block elements** in the middle of the table result from the filling of d orbitals; and the lanthanide/actinide **f-block elements** detached at the bottom of the table result from the filling of f orbitals.

Periodic properties: The arrangement of the periodic table reveals trends in the properties of the elements. A **trend** is a predictable change in a particular direction. **Atomic radii** *increase* going down a group of the periodic table, but *decrease* going across a row from left to right.

The amount of energy necessary to remove the highest-energy electron from an isolated neutral atom in the gaseous state is called the atom's **ionization energy**. Ionization energy tends to *decrease* down a group, and generally *increases* from left to right across a row of the periodic table.

Electronegativity is the ability of an atom in a molecule to attract the shared electrons in a covalent bond. Electronegativity *increases* from left to right and generally *decreases* from top the bottom.

1.3. Chemical Bonds

Types of chemical bonds: intramolecular interactions as ionic, covalent, metallic bonds and intermolecular interactions, as London dispersion forces, dipole-dipole forces, hydrogen bonds.

A **molecule** is the smallest particle in a chemical element or compound that has the chemical properties of that element or compound. Molecules are made up of atoms that are held together by chemical bonds.

Empirical formula is a chemical formula that shows the composition of a compound in terms of the relative numbers and kinds of atoms in the simplest ratio.

Molecular formula is a chemical formula that shows the number and kinds of atoms in a molecule, but not the arrangement of the atoms.

Octet rule is a concept of chemical bonding theory that is based on the assumption that atoms tend to have either empty valence shells or full valence shells of eight electrons.

An **ionic bond** results from a *transfer* of one or more electrons from one atom to another. **Ion** is an atom, radical, or molecule that has gained or lost one or more electrons and has a negative or positive charge. **Cation** is an ion that has a positive charge, **anion** is an ion that has a negative charge. Ionic bonds form between ions of opposite charge. The ions in a salt crystal form repeating patterns, with each ion held in place because there are more attractive forces than repulsive ones. **Crystal lattice** is the regular pattern in which a crystal is arranged. **Unit cell** is the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice. Charged, covalently bonded *groups* of atoms, called **polyatomic ions**, also exist (for example, ammonium ion, hydroxide ion, nitrate ion and the doubly charged sulphate ion). These polyatomic ions as charged molecules because they consist of specific numbers and kinds of atoms joined together by covalent bonds in a definite way, with the overall unit having a positive or negative charge.

Covalent bond is a bond formed when atoms share one or more pairs of electrons. The shared electrons move in the space surrounding the nuclei of the two atoms. The space that these shared electrons moves within is called a molecular orbital. **Molecular orbital** is the region of high probability that is occupied by an individual electron as it travels with a wavelike motion in the three-dimensional space around one of two or more associated nuclei. **Bond length** is the distance between two bonded atoms at their minimum potential energy; the average distance between the nuclei of two bonded atoms. **Bond energy** is the energy required to break the bonds in 1 mol of a chemical compound. **Nonpolar covalent bond** is a covalent bond in which the bonding electrons are equally attracted to both bonded atoms; **polar covalent bond** is a covalent bond in which a shared pair of electrons is held more closely by one of the atoms. **Dipole** is a molecule or part of a molecule that contains both positively and negatively charged regions. The difference in electronegativity between the atoms connected to the covalent bond in the molecule indicates the apolar or polar nature of the binding. If the difference of electronegativity is less than 0.6, the bond is substantially apolar covalent, if it is between 0.6 and 2.1, it is polar covalent when greater than 2.1 is an ion binding.

Both ionic and covalent bonds involve valence electrons, the electrons in the outermost energy level of an atom. **Valence electron** is an electron that is found in the outermost shell of an atom and that determines the atom's chemical properties. **Lewis structure** is a structural formula in which electrons are represented by dots; dot pairs or dashes between two atomic symbols represent pairs in covalent bonds. The **unshared pair** is a nonbonding pair of electrons in the valence shell of an atom; also called *lone pair*. The **single bond** is a covalent bond in which two atoms share one pair of electrons. In **double bond** two atoms share two pairs of electrons. In **triple bond** two atoms share three pairs of electrons. Electron pairs can determine molecular shapes, as linear, bent, trigonal planar or tetrahedral geometry. Molecular shape affects a substance's properties, because the shape affects polarity and polarity affects properties.

Bonding in metals: Some properties, such as hardness and melting point, vary considerably among metals, but other properties are characteristic of metals in general. For instance, all metals can be drawn into wires (ductility) or beaten into sheets (malleability) without breaking into pieces like glass or an ionic crystal. Furthermore, all metals have a high

thermal and electrical conductivity. When you touch a metal, it feels cold because the metal efficiently conducts heat away from your hand, and when you connect a metal wire to the terminals of a battery, it conducts an electric current.

In a metal crystal the valence electrons can't be localized in a bond between any particular pair of atoms, they are delocalized and belong to the crystal as a whole. In the **electron-sea model**, a metal crystal is viewed as a three-dimensional array of metal cations immersed in a sea of delocalized electrons that are free to move throughout the crystal. The continuum of delocalized, mobile valence electrons acts as an electrostatic glue that holds the metal cations together.

Intermolecular forces are the forces of attraction between molecules. These forces are of several different types, including *London dispersion forces*, *dipole–dipole forces* and *hydrogen bonds*. The approximate energy of the interaction is 0.1 to 10 kJ / mol for the former two and 10 to 50 kJ / mol for the hydrogen bond. The primary chemical bonds are much stronger, the ionic or covalent bonds have energy of 100-1000 kJ / mol.

Properties depend on types of intermolecular force: The differences in the properties of the substances are related to the differences in the types of forces that act within each substance.

London dispersion forces are the intermolecular attraction resulted from the motion of electrons and the creation of temporary dipoles. Temporary dipoles in molecules cause forces of attraction between the molecules.

Dipole–dipole forces are the result of electrical interactions among dipoles on neighbouring molecules. In dipole-dipole forces, the positive end of one molecule attracts the negative end of a neighbouring molecule. Bonds are polar because atoms of differing electronegativity are bonded together. The greater the difference in electronegativity in a diatomic molecule, the greater the polarity is.

Hydrogen bonds can form with a hydrogen atom that is covalently bonded to very electronegative atoms as fluorine, oxygen and nitrogen.. When a hydrogen atom bonds to an atom of N, O, or F, the hydrogen atom has a large, partially positive charge. The partially positive hydrogen atom of polar molecules can be attracted to the unshared pairs of electrons of neighbouring molecules. The hydrogen bond between the molecules of the HF is the strongest since the fluorine atom is the most electronegative element.

1.4. States of Matter

Different forms of matter: All the many kinds of matter can be classified as either *pure substances* or *mixtures*. Pure substances, in turn, can be either elements or *chemical compounds*.

Chemical compound is a pure substance that is formed when atoms of two or more different elements combine and create a new material with properties completely unlike those of its constituent elements. A compound has a constant composition throughout, and its constituent units are all identical. A compound is written by giving its **chemical formula**, which lists the symbols of the individual constituent elements and indicates the number of atoms of each. **Atoms, ions, and molecules** are very small, so even tiny samples have a huge number of particles. To make counting such large numbers easier, scientists use the same approach to represent the number of ions or molecules in a sample as they use for atoms. The SI unit for amount is called the **mole** (mol). A mole is the number of atoms in exactly 12 grams of carbon-12. The number of particles in a mole is called **Avogadro's number** or Avogadro's

constant: 6.022×10^{23} , the number of atoms or molecules in 1.000 mol. **Molar mass** is the mass in grams of one mole of a substance.

Mixtures, unlike chemical compounds, whose constituent units are identical, these are simply blends of two or more substances added together in some random proportion without chemically changing the individual substances themselves. Mixtures can be further classified as either *heterogeneous* or *homogeneous*.

Heterogeneous mixtures are those in which the mixing is not uniform and which therefore have regions of different composition. **Homogeneous mixtures** are those in which the mixing is uniform and which therefore have a constant composition throughout.

Physical variables: The gaseous state of the materials with three status indicators, pressure (P), volume (V) and temperature (T) can be clearly characterized by gas with the same number of molecules (n). Pressure (P) is measured in pascals (Pa), sometimes expressed as newtons per square metre ($\text{N}\cdot\text{m}^{-2}$); volume (V) is measured in m^3 ; temperature (T) has to be in kelvins (K), add 273.15 if you are given a Celsius temperature; number of moles (n), the units are mol.

The Gas Laws: The specific relationships among the four physical variables are called the **gas laws**, and a gas whose behaviour follows the laws exactly is called an **ideal gas**.

Boyle's law: the volume of an ideal gas varies inversely with pressure. That is, P times V is constant when n and T are kept constant: $PV = k$, at constant n and T .

Charles' law: the volume of a fixed amount of an ideal gas at a constant pressure varies directly with its absolute temperature: $V/T = k$ at constant n and P .

Avogadro's law: the volume of an ideal gas at a fixed pressure and temperature depends on its molar amount. If the amount of the gas is halved, the gas volume is halved; if the amount is doubled, the volume is doubled: $V/n = k$ at constant T and P .

All three of the gas laws can be combined into a single statement called the **ideal gas law**, which describes how the volume of a gas is affected by changes in pressure, temperature, and amount. When the values of any three of the variables P , V , T , and n are known, the value of the fourth can be calculated using the ideal gas law. The constant R in the equation is called the **gas constant** and has the same value for all gases: $PV = nRT$. Standard temperature and pressure (STP) for gases $T = 273\text{K}$, $P = 0.1\text{MPa}$

Crystalline solids are those whose atoms, ions, or molecules have an ordered arrangement extending over a long range. This order on the atomic level is also seen on the visible level because crystalline solids usually have flat faces and distinct angles. **Amorphous solids**, by contrast, are those whose constituent particles are randomly arranged and have no ordered long-range structure. Rubber is an example. Crystalline solids can be further categorized as *ionic*, *molecular*, *covalent network*, or *metallic*. **Ionic solids** are those like sodium chloride, whose constituent particles are ions. A crystal of sodium chloride is composed of alternating and ions ordered in a regular three-dimensional arrangement and held together by ionic bonds. **Molecular solids** are those like sucrose or ice, whose constituent particles are molecules held together by the intermolecular forces. A crystal of ice, for example, is composed of molecules held together in a regular way by hydrogen bonding. **Covalent network solids** are those like quartz or diamond, whose atoms are linked together by covalent bonds into a giant three-dimensional array. In effect, a covalent network solid is one very large molecule. **Metallic solids**, such as silver or iron, also consist of large arrays of atoms, but their crystals have metallic properties such as electrical conductivity.

Phase changes of matter: Most of the substances can be in three states, as solid, liquid, and gas. The physical properties of each state come from the arrangement of particles which

depends on the temperature and the pressure. The physical properties of each state of matter come from the arrangement of particles. All state changes are physical changes, because the identity of the substance does not change, while the physical form of the substance does change. *Freezing* is the change of state in which a liquid becomes a solid. *Melting* is the change of state in which a solid becomes a liquid. *Evaporation*, the change of state in which a liquid becomes a gas. *Condensation* is the change of state in which a gas becomes a liquid. But solids can evaporate, too. A thin film of ice on the edges of a windshield can become a gas by *sublimation* as the car moves through the air. Gases become solids by a process sometimes called *deposition*. The temperature at which boiling occurs when the external pressure is exactly 0.1 MPa is called the **normal boiling point** of the liquid. The boiling points depend on the magnitude of the intermolecular forces present and on the temperature. The smaller the intermolecular forces, the boiling point because loosely held molecules escape more easily. The higher the temperature, the higher the boiling point because a larger fraction of molecules have sufficient kinetic energy to escape for boiling.

Solutions: homogeneous mixtures can be classified according to the size of their constituent particles as either *solutions* or *colloids*. **Solutions**, the most important class of homogeneous mixtures, contain particles with diameters in the range 0.1–2 nm, the size of a typical ion or small molecule. They are transparent, although they may be colored, and they do not separate on standing. **Colloids**, such as milk and fog, contain particles with diameters in the range 2–500 nm. Although they are often murky or opaque to light, they do not separate on standing. Mixtures called **suspensions** also exist, having even larger particles than colloids. These are not truly homogeneous, however, because their particles separate on standing and are visible with a low-power microscope. Blood, paint, and aerosol sprays, are examples.

Concentration of solutions: In a solution, the solute is distributed evenly throughout the solvent. This means that any part of a solution has the same ratio of solute to solvent as any other part of the solution. This ratio is the **concentration** of the solution. Concentrations can be expressed in many forms. The **percentage by mass** gives the mass of dissolved substance the percentage of mass of solution:

$$\% \text{ mass} = \frac{\text{mass of solute (g)}}{\text{mass of solution(g)}} \times 100$$

One unit of concentration used in pollution measurements that involve very low concentrations is **parts per million**, or **ppm**. Parts per million is the number of grams of solute in 1 million grams of solution. For example, the concentration of lead in drinking water may be given in parts per million. It is often convenient for chemists to discuss concentrations in terms of the number of solute particles in solution rather than the mass of particles in solution. Since the mole is the unit chemists use to measure the number of particles, they often specify concentrations using **molarity**. Molarity describes how many moles of solute are in each liter of solution. Suppose that 0.30 moles of KBr are present in 0.40 L or dm³ of solution. The molarity of the solution is calculated as follows: $c = 0.75 \text{ M KBr}$

The symbol M is read as “molar” or as “moles per liter or dm³.” Any amount of this solution has the same ratio of solute to solution.

Solubility: Polar compounds tend to dissolve in other polar compounds, and nonpolar compounds tend to dissolve in other nonpolar compounds. The rule is “**like dissolves like**”. Nonpolar molecules are generally also soluble with each other.

Even two polar liquids placed in the same container may not dissolve in each other rapidly. Their strong intermolecular forces can only act on nearby molecules—not between

molecules at the top of the container and those at the bottom. The speed of the process can be increased by **shaking the mixture**. This action breaks the two liquids into small droplets and thereby increases the amount of contact between the surfaces of the liquids. This process works because the only place that dissolving can occur is at the surface between the two liquids, where the different molecules are near each other.

Similarly, in considering the solubility of solids in liquids, the only place where dissolution can occur is at **the surface of the solid particles**. The solid must be broken into smaller particles and then into molecules or ions, which can form a solution with the solvent molecules.

Another way to make most solids dissolve more and faster is **to increase the temperature**. Increasing the temperature is effective because, in general, solvent molecules with greater kinetic energy can dissolve more solute particles. In most cases, such as in the case of KNO_3 , the solubility increases with temperature. However, temperature has little effect on the solubility of NaCl . The solubility of Li_2SO_4 actually decreases slightly as temperature increases.

When the maximum amount of solute is dissolved in a solution, the solution is said to be a **saturated solution**. If a solution is saturated, any additional solute that is added collects at the bottom of the container. If more solute can be added to a solution and dissolve, the solution is considered to be an **unsaturated solution**. In a saturated solution, some excess solute remains undissolved, and the mass that dissolves is equal to the solubility value for that temperature. **Supersaturated solution** a solution holding more dissolved solute than what is required to reach equilibrium at a given temperature.

1.5. Thermochemistry

Energy is the capacity to supply heat or do work: Energy = Heat + Work

The SI energy unit is given the name **joule (J)**.

The conservation of energy law: energy can be neither created nor destroyed; it can only be converted from one form into another.

Thermal energy is the kinetic energy of molecular motion, which we measure by finding the temperature of an object.

Temperature is a measure of how hot (or cold) something is; specifically, a measure of the average kinetic energy of the particles in an object. Temperature is an *intensive property*, which means that the temperature of a sample does not depend on the amount of the sample.

Heat is the energy transferred between objects that are at different temperatures. Heat is an *extensive property* which means that the amount of energy transferred as heat by a sample depends on the amount of the sample.

Chemical energy is a kind of potential energy in which chemical bonds act as the “storage” medium.

When keeping track of the energy changes that occur in a chemical reaction, it's helpful to think of the reaction as separate from the world around it. The substances we focus on in an experiment—the starting reactants and the final products—are collectively called the **system**, while everything else—the reaction flask, the room, the building, and so on—is called the **surroundings**. If the system were somehow isolated from its surroundings so that no energy transfer could occur between the two, then the total **internal energy (E)** of the system—the sum of all the kinetic and potential energies for every molecule or ion in the system—would be conserved and remain constant throughout the reaction. In fact, this assertion is just a

restatement of the **first law of thermodynamics**: The total internal energy of an isolated system is constant.

The energy change represents the difference in internal energy between the final and initial states of the system: $\Delta E = E_{\text{final}} - E_{\text{initial}}$

Expansion work done during a chemical reaction is calculated by the formula, $w = -P\Delta V$, where P is the external pressure opposing the change in volume.

Enthalpy, which is represented by the symbol H , is the sum of the internal energy of a system plus the product of the system's volume multiplied by the pressure that the system exerts on its surroundings:

$$\Delta H = \Delta E + P\Delta V$$

Enthalpy change can be positive, which means that the heating of a sample requires energy. So, the heating of a sample is an **endothermic process**. In contrast the cooling of sample releases energy or has a negative enthalpy change and is an **exothermic process**. Processes that have positive enthalpy changes are endothermic and processes that have negative enthalpy changes are exothermic.

The thermodynamic standard state has been defined as a most stable form of a substance at 0.1 MPa (1 atm) pressure and at a specified temperature, usually 25°C; 1 M concentration for all substances in solution.

ΔH° is the standard state ΔH° . Enthalpy change is often called a *heat of reaction* because it is a measure of the heat flow into or out of a system at constant pressure.

The value of given **ΔH° for a chemical equation** assumes that the equation is balanced for the number of moles of reactants and products, that all substances are in their standard states, and that the physical state of each substance is as specified. The actual amount of heat released in a specific reaction depends on the amounts of reactants. The enthalpy change for one mole of a pure substance is called **molar enthalpy change**.

The enthalpy change in forming 1 mol of a substance from elements in their standard states is called the **standard enthalpy of formation** of the substance, ΔH_f° . Note that the values of the standard enthalpies of formation for elements are 0. From a list of standard enthalpies of formation, the enthalpy change of any reaction for which data is available can be calculated.

1.6. Chemical Kinetics

The area of chemistry concerned with reaction rates and the sequence of steps by which reactions occur is called **chemical kinetics**.

The rate of a reaction quantitatively shows how fast the concentration of a reactant or a product changes per unit time: $\text{Rate} = \text{Concentration change} / \text{Time change}$.

The reaction rate can be defined either as the *increase* in the concentration of a *product* per unit time or as the *decrease* in the concentration of a *reactant* per unit time. Concentration, pressure, temperature, and surface area are the most important factors on which the rate of a chemical reaction depends. **The rate of a chemical reaction increases as the concentration of a reactant increases**. Reaction rates decrease with time because the reaction rate depends on the concentration of the reactants. As the reaction proceeds, the reactant is consumed and its concentration declines. This change in concentration, in turn, decreases the reaction rate.

All chemical reactions are affected by temperature. In almost every case, **the rate of a chemical reaction increases with increasing temperature**. Collisions between molecules (or other particles, such as ions or atoms) are necessary for a reaction to occur. Rise in temperature increases the number of collisions and thereby boosts the reaction rate. Only the

molecules with especially high kinetic energy are likely to react. The minimum energy that a pair of colliding molecules (or atoms or ions) needs to have before a chemical change becomes a possibility is called **activation energy of the reaction**. It is represented by the symbol E_a . No reaction is possible if the colliding pair has less energy than E_a .

Adding substances called catalysts to a reaction mixture will increase the reaction rate, even though the catalyst is still present and unchanged at the end of the reaction. **Catalyst** is a substance that changes the rate of a chemical reaction without being consumed or changed significantly. **Catalysis** is the acceleration of a chemical reaction by a catalyst. **Catalysts lower the activation energy**. Catalysis works by making a different pathway available between the reactants and the products. This new pathway has a different mechanism and a different rate law from that of the uncatalyzed reaction.

1.7. Chemical Equilibrium

Completion reactions run until one of the reactants runs out: formation of a gas that is allowed to escape; formation of a precipitate, which is a solid that makes the equation heterogeneous and essentially eliminates the product.

Reversible reactions do not go to completion and occur in both the forward and reverse direction. In reversible reaction the products re-form the original reactants. The forward and reverse reactions take place at the same time. Reactions in which the forward and reverse reaction rates are equal are at chemical equilibrium. **Chemical equilibrium** is a state of balance in which the rate of a forward reaction equals the rate of the reverse reaction and the concentrations of products and reactants remain unchanged. Chemical equilibrium is different from static equilibrium because it is dynamic. In a *dynamic equilibrium*, there is no net change in the system. Two opposite changes occur at the same time in a dynamic equilibrium. In a chemical equilibrium, an atom may change from being a part of the products to being a part of the reactants many times. But the overall concentrations of products and reactants stay the same.

Equilibrium constant, K_{eq} is a number that relates the concentrations of starting materials and products of a reversible chemical reaction to one another at a given temperature.

Determining K_{eq} for reactions at chemical equilibrium: $a A + b B \rightleftharpoons c C + d D$

1. Write a balanced chemical equation.
 - Make sure that the reaction is at equilibrium before you write a chemical equation.
2. Write an equilibrium expression.
 - To write the expression, place the product concentrations in the numerator and the reactant concentrations in the denominator.
 - The concentration of any solid or a pure liquid that takes part in the reaction is left out because these concentrations never change.
 - For a reaction occurring in aqueous solution, water is omitted because the concentration of water is almost constant during the reaction.
3. Complete the equilibrium expression.
 - To complete the expression, raise each substance's concentration to the power equal to the substance's coefficient in the balanced chemical equation: **Equilibrium constant expression:**

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Chemical equilibrium respond to three kinds of stress: changes in the concentrations of reactants or products, changes in temperature, and changes in pressure. When a stress is first applied to a system, any chemical equilibrium is disturbed. As a result, the rates of the forward and backward reactions in the system are no longer equal. The system responds to the stress by forming more products or by forming more reactants. A new chemical equilibrium is reached when enough reactants or products form. At this point, the rates of the forward and backward reactions are equal again.

Le Châtelier's principle: If a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. This principle states that a system in equilibrium will oppose a change in a way that helps eliminate the change.

1. When equilibrium is disturbed by the **addition or removal of any reactant or product**, Le Châtelier's principle predicts that

- The concentration stress of an *added* reactant or product is relieved by net reaction in the direction that *consumes* the added substance.
- The concentration stress of a *removed* reactant or product is relieved by net reaction in the direction that *replenishes* the removed substance.

2. When an equilibrium is disturbed by the **change of pressure or volume**, Le Châtelier's principle predicts that

- An *increase* in pressure by reducing the volume will bring about net reaction in the direction that *decreases* the number of moles of gas.
- A *decrease* in pressure by enlarging the volume will bring about net reaction in the direction that *increases* the number of moles of gas.

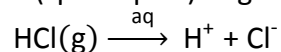
3. The **temperature dependence** of the equilibrium constant depends on the sign of ΔH° for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH°) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH°) increases as the temperature increases.

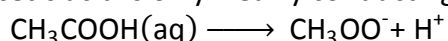
4. The addition of a catalyst equally affects the rate of the forward and of the reverse reaction; hence, **a catalyst does not change the equilibrium mixture or the value of the equilibrium constant, K .**

1.8. Aqueous Equilibria: Acids and Bases

Substances such as NaCl or KBr, which dissolve in water to produce conducting solutions of ions, are called **electrolytes**. Substances such as sucrose or ethyl alcohol, which do not produce ions in aqueous solution, are called **nonelectrolytes**. Most electrolytes are ionic compounds, but some are molecular. Hydrogen chloride, for example, is a molecular compound when pure but **dissociates** (splits apart) to give ions when it dissolves in water.



Compounds that dissociate to a large extent (70–100%) into ions when dissolved in water are said to be **strong electrolytes**, while compounds that dissociate to only a small extent are **weak electrolytes**. Potassium chloride and most other ionic compounds, for instance, are largely dissociated in dilute solution and are thus strong electrolytes. Acetic acid, by contrast, dissociates to the extent of about 1.3% in a 0.10 M solution and is a weak electrolyte. As a result, a 0.10 M solution of acetic acid is only weakly conducting.



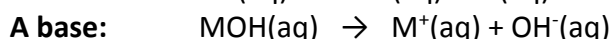
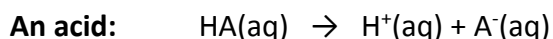
The strength of the electrolytes can be characterized by the degree of dissociation (α):

$$\text{"degree of dissociation" ("}\alpha\text{")} = \frac{([\text{"ionized solute"}])}{([\text{"all solute"}])}$$

The dissociation rates of the electrolytes vary between 0 and 1. The degree of dissociation depends on the material quality and concentration of the electrolytes. The strong electrolytes have a dissociation degree of 1 and the nonelectrolytes are 0 regardless of their concentration. The dissociation degree of weak electrolytes varies between 0 and 1 depending on the concentration.

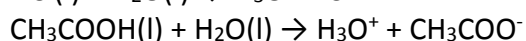
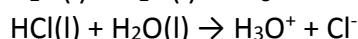
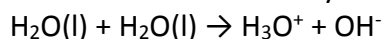
The characteristic properties of acids and bases have been known for centuries. **Acids** react with metals such as iron and zinc to yield H_2 gas, and they change the colour of the plant dye *litmus* from blue to red. By contrast, **bases** feel slippery, and they change the colour of litmus from red to blue. When acids and bases are mixed in the right proportion, the characteristic acidic and basic properties disappear, and new substances known as **salts** are obtained.

Arrhenius proposed that acids are substances that dissociate in water to produce hydrogen ions and those bases are substances that dissociate in water to yield hydroxide ions



In these equations, HA is a general formula for an acid—for example, HCl or —and MOH is a general formula for a metal hydroxide—for example, NaOH or KOH.

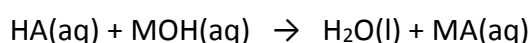
As bare hydrogen nucleus (proton) with no electron nearby, H^+ is much too reactive to exist by itself. Rather, the H^+ attaches to a water molecule, giving the more stable trigonal pyramidal **hydronium ion, H_3O^+** , and it can associate through hydrogen bonding with additional three water molecules. The ionization of water and the dissociation of water-dissolving agents to H^+ are described by the following equations:



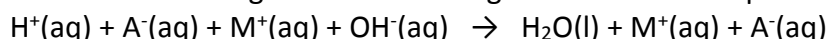
Different acids dissociate to different extents in aqueous solution. Those acids that dissociate to a large extent are strong electrolytes and **strong acids**; those acids that dissociate only to a small extent are weak electrolytes and **weak acids**. For example, that HCl, HClO_4 , and H_2SO_4 are strong electrolytes and therefore strong acids, whereas CH_3COOH and HF are weak electrolytes and therefore weak acids.

Bases, like acids, can also be either strong or weak, depending on the extent to which they dissociate and produce OH^- ions in aqueous solution. Most metal hydroxides, such as NaOH and Ba(OH)_2 are strong electrolytes and **strong bases**, but ammonia (NH_3) is a weak electrolyte and a **weak base**. Ammonia is weakly basic because it reacts to a small extent with water to yield NH_4^+ and OH^- ions.

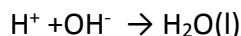
When an acid and a base are mixed in the right stoichiometric proportion, both acidic and basic properties disappear because of a **neutralization reaction**, which produces water and a *salt*. The anion of the salt (A^-) comes from the acid, and the cation of the salt (M^+) comes from the base:



Because salts are generally strong electrolytes in aqueous solution, we can write the neutralization reaction of a strong acid with a strong base as an ionic equation:



These neutralisation reactions are simplified by the formation reaction of water from ions:



According to the **Brønsted–Lowry theory**, an acid is any substance (molecule or ion) that can transfer a proton (ion) to another substance, and a base is any substance that can accept a proton. In short, acids are proton donors, bases are proton acceptors, and acid–base reactions are proton-transfer reactions:

Brønsted–Lowry acid: A substance that can transfer H^+ .

Brønsted–Lowry base: A substance that can accept H^+ .

Chemical species whose formulas differ only by one proton are said to be **conjugate acid–base pairs**. Thus, A^- is the **conjugate base** of the acid HA , and HA is the **conjugate acid** of the base A^- . Similarly, BH^+ is the conjugate base of the acid BH^+ and BH^+ is the conjugate acid of the base B .

Amphoteric describes a substance, such as water, that has the properties of an acid and of a base.

The dissociation of water: $2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$. This reaction is characterized by the equilibrium equation: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

The concentration of water is omitted from the equilibrium constant expression because, as a pure liquid, its concentration is a constant that is incorporated into the equilibrium constant. The equilibrium constant is called the **ion-product constant for water**.

The H_3O^+ and the OH^- concentrations in pure water are the same, $1.0 \times 10^{-7} \text{ M}$ at 25°C . The numerical value of K_w at 25°C is 1.0×10^{-14} at 25°C .

We can distinguish acidic, neutral, and basic aqueous solutions by the relative values of the H_3O^+ and the OH^- concentrations:

acidic:	$[\text{H}_3\text{O}^+] > [\text{OH}^-];$
neutral:	$[\text{H}_3\text{O}^+] = [\text{OH}^-];$
basic:	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$

At 25°C , $[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \text{ M}$ in an acidic solution, $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$ in a neutral solution, and $[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \text{ M}$ in a basic solution.

The concentration of hydronium ions in a solution expresses its *acidity*. The concentration of hydroxide ions in a solution expresses its *basicity*. When acidity and basicity are exactly balanced such that the numbers of H_3O^+ and OH^- ions are equal, we say that the solution is *neutral*. Pure water is neutral because it contains equal amounts of the two ions.

pH: Sørensen proposed using the negative of the power of 10 (that is, the negative logarithm) of $[\text{H}_3\text{O}^+]$ as the index of basicity and acidity. He called this measure the pH. The letters *p* and *H* represent **power of hydrogen**. The pH is a negative logarithmic scale, a *lower* pH reflects a *higher* hydronium ion concentration. A **pH** of 7 is neutral, a pH of less than 7 is acidic, and a pH of greater than 7 is basic.

Determination pH of the solutions: Certain dyes, known as **indicators**, turn different colours in solutions of different pH. Some indicators, such as litmus, are natural products, but most are synthetic. Each indicator has its own colours and its individual range of pH over which it changes shade. Using acid–base indicators is quick and convenient, but does not give very precise results. A pH meter is an electrochemical instrument that can measure pH accurately.

1.9. Electrochemistry

Oxidation is a reaction that removes one or more electrons from a substance such that the substance's valence or oxidation state increases.

Reduction is a chemical change in which electrons are gained, either by the removal of oxygen, the addition of hydrogen, or the addition of electrons.

Oxidation-reduction reaction is any chemical change in which one species is oxidized (loses electrons) and another species is reduced (gains electrons); also called *redox reaction*.

Oxidation number is the number of electrons that must be added to or removed from an atom in a combined state to convert the atom into the elemental form.

Assigning oxidation numbers:

1. Identify the formula.

- If no formula is provided, write the formula of the molecule or ion.

2. Assign known oxidation numbers.

• Place an oxidation number above each element's symbol according to the following rules.

a. The oxidation number of an atom of any free (uncombined) element in atomic or molecular form is zero.

b. The oxidation number of a monatomic ion is equal to the charge on the ion.

c. The oxidation number of an atom of fluorine in a compound is always -1 because it is the most electronegative element.

d. An atom of the more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.

e. In compounds, atoms of the elements of Group 1, Group 2, and aluminum have positive oxidation numbers of +1, +2, and +3, respectively.

f. The oxidation number of each hydrogen atom in a compound is +1, unless it is combined with a metal atom; then it is -1.

g. The oxidation number of each oxygen atom in compounds is usually -2. When combined with fluorine atoms, oxygen becomes +2. In peroxides, such as H_2O_2 , an oxygen atom has an oxidation number of -1.

3. Calculate remaining oxidation numbers, and verify the results.

• Use the total oxidation number of each element's atoms (the oxidation number for an atom of the element multiplied by the subscript for the element) and the following rules to calculate missing oxidation numbers.

h. The sum of the oxidation numbers for all the atoms in a molecule is zero.

i. The sum of the oxidation numbers for all atoms in a polyatomic ion is equal to the charge on that ion.

In a redox reaction, the oxidation numbers of atoms that are oxidized increase, and those of atoms that are reduced decrease. Substances that cause the oxidation of other substances are called **oxidizing agents**. They accept electrons easily and so are reduced. Common oxidizing agents are oxygen, hydrogen peroxide, and halogens. **Reducing agents** cause reduction to happen and are themselves oxidized. The iron(II) ion caused the reduction of the permanganate ion and was the reducing agent. Common ones are metals, hydrogen, and carbon.

Electrochemistry is the branch of chemistry that is the study of the relationship between electric forces and chemical reactions.

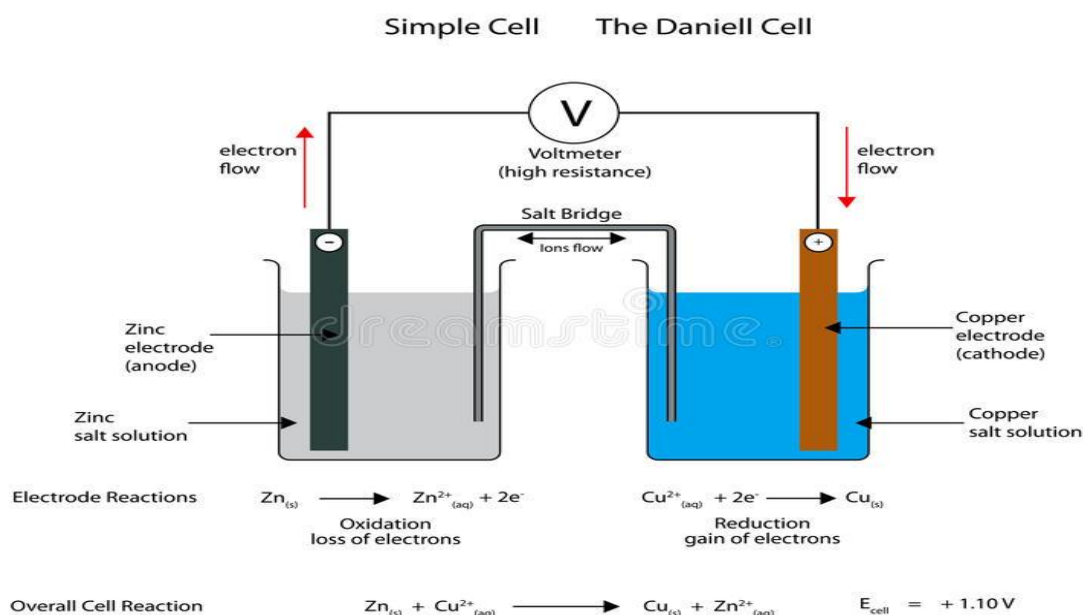
Electrical "pressure," often called *electric potential*, or is **voltage**, expressed in units of *volts*. **Voltage** is the potential difference or electromotive force, measured in volts; it represents the amount of work that moving an electric charge between two points would take.

The movement of electrons or other charged particles is described as *electric current* and is expressed in units of *amperes*.

An **electrochemical cell** consists of two electrodes separated by an electrolyte. An **electrode** is a conductor that connects with a non-metallic part of a circuit, such as an electrolyte.

Electrode reactions happen on the surfaces of electrodes. **Cathode** is the electrode on whose surface reduction takes place. **Anode** is the electrode on whose surface oxidation takes place; anions migrate toward the anode, and electrons leave the system from the anode. Although the two electrode reactions occur at the same time, they occur at different places in the cell.

A battery is one kind of **galvanic cell**, a device that can change chemical energy into electrical energy. In these cells, a spontaneous reaction happens that causes electrons to move. Daniell cells were used as energy sources in the early days of electrical research. There



are many other kinds of galvanic cells. These include dry cells, lead-acid batteries, and fuel cells.

Using one electrode as a standard and determining electrode potentials in reference to that standard is much easier than measuring the potential between every combination of electrodes is. The electrode that has been chosen as a standard is the **standard hydrogen electrode** (SHE). It consists of a platinum electrode in a 1.00 M H_3O^+ solution in the presence of H_2 gas at 0.1 MPa pressure and 25°C. The SHE is assigned a potential of 0.0000 V and its reaction is $2\text{H}_3\text{O}^+(aq) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{H}_2\text{O}(l)$.

When measuring potentials, a salt bridge, a narrow tube filled with a concentrated solution of a salt, must be used to link the compartments. When a SHE is joined to another electrode by a salt bridge, a voltmeter can be used to determine the **standard electrode potential**, E° , for the electrode.

The standard electrode potential is sometimes called the **standard reduction potential** because it is listed by the reduction half-reactions. However, a voltmeter allows no current in the cell during the measurement. Therefore, the conditions are neither galvanic nor electrolytic—the cell is at equilibrium. As a result, the half-reactions listed in the table are

shown as reversible. If the reaction occurs in the opposite direction, as an oxidation half-reaction, E° will have the opposite sign.

Standard electrode potential is the potential developed by a metal or other material immersed in an electrolyte solution relative to the potential of the hydrogen electrode, which is set at zero

Calculating the voltage of a cell: Think of E° is as a measure of the ability of an electrode to gain electrons. A more positive value means the electrode is more likely to be a cathode. The standard cell voltage—the voltage of a cell under standard conditions— can be found by subtracting the standard potentials of the two electrodes, as follows:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

To determine the reaction that will happen naturally, use the electrode with the most positive E° value as the cathode, as shown in Sample Problem. Otherwise, a given reaction happens naturally if E°_{cell} is positive. If E°_{cell} is negative, the reaction could be made to happen if energy is added.

Electrolysis the process in which an electric current is used to produce a chemical reaction, such as the decomposition of water. Galvanic cells generate electrical energy, but another kind of cell *consumes* electrical energy. In an **electrolytic cell**, chemical changes are brought about by driving electrical energy through an electrochemical cell. In fact, the words *electrolysis* and *electrolytic* mean “splitting by electricity” and electrolysis does refer to the decomposition of a compound, usually into its elements. However, many changes other than decomposition can happen when you use an electrolytic cell. During the electrolyses anions go to the “+” anode, and oxidation happens on the anode, while cations go to the “-” cathode, and reduction happens on the cathode.

Michael Faraday observed that the masses of the substances produced in an electrochemical reaction depend on the amount of current transferred at the electrode. The electrical charge on one mole of electrons is called the faraday in his honour. The electrical charge carried by one mole of electrons is one faraday. In a given electrolysis reaction, the mass of the product formed or reactant consumed is proportional to the quantity of charge (Q in coulombs) passed through the cell. One mole of electrons has a charge of 96,500 coulombs which equals one Faraday (F).

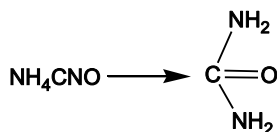
Corrosion of iron (rusting) is an electrochemical process in which iron is oxidized in an anode region of the metal surface and oxygen is reduced in a cathode region. Corrosion can be prevented by covering iron with another metal, such as zinc, in the process called **galvanizing**, or simply by putting the iron in electrical contact with a second metal that is more easily oxidized, a process called **cathodic protection**.

2. ORGANIC Chemistry

2. 1. General Characteristics of organic compounds

2.1.1. The concept of organic matter

Friedrich Wöhler prepared urea by heating ammonium cyanate (NH_4CNO), a compound obtained from nonliving materials.



Although we still use the term organic, it no longer distinguishes between compounds of living or nonliving origin. ***Organic chemistry is the chemistry of compounds containing carbon.***

2.1.2. Classification of organic compounds

- Organic compounds containing only C and H atoms are called **hydrocarbons**.
- Compounds having functional groups in their structure are classified by their functional groups.

Functional groups

The ***functional groups*** are ***reactive portions*** of the molecule that undergo reactions predictable from the structure of atom or group joining the carbon atom.

Organic compounds are considered for classification purposes to be derived from hydrocarbons by replacing hydrogen atom(s) in hydrocarbons by certain ***atoms or groups of atoms (functional groups)***.

Functional groups in organic compounds

Compound	Name of the functional group	Compound name
$R-X$	halo	Alkyl halide
$R-O-H$	hydroxyl	Alcohol
$Ar-O-H$	hydroxyl	Phenol
$R-O-R$	alkoxy	Ether
$\begin{array}{c} O \\ // \\ R-C \\ \backslash \\ H \end{array}$	aldehyde (or formyl)	Aldehyde
$\begin{array}{c} R \\ \backslash \\ C=O \\ / \\ R \end{array}$	carbonyl (keto or oxo)	Ketone
$R-NH_2$	amino	Amine
$\begin{array}{c} O \\ // \\ R-C \\ \backslash \\ OH \end{array}$	carboxyl	Carboxylic acid
$\begin{array}{c} O \\ // \\ R-C \\ \backslash \\ NH_2 \end{array}$	amido	Amide
$\begin{array}{c} O \\ // \\ R-C \\ \backslash \\ X \end{array}$	carbonyl halide	Acyl halide
$\begin{array}{c} R-C-O-C-R \\ // \quad // \\ O \quad O \end{array}$	anhydride	Carboxylic acid anhydride
$\begin{array}{c} O \\ // \\ R-C \\ \backslash \\ O-R \end{array}$	ester	Ester
$R-NO_2$	nitro	Nitroalkane
$\begin{array}{c} O \\ \\ R-S-OH \\ \\ O \end{array}$	sulfonic acid	Sulfonic acid
$R-C \equiv N$	cyano	Nitrile

2.1.3. Organic chemical reactions

Addition reactions

Substitution reactions

Elimination reactions

Organic redox reactions

ORGANIC COMPOUNDS

nomenclature, isomerism, physical state and molecular structure, properties, chemical reactions, occurrence, use, physiological effect

2.2 Hydrocarbons The simplest organic compounds are **hydrocarbons**, compounds containing only carbon and hydrogen.

Hydrocarbons in which all carbon-carbon bonds are single bonds (**saturated hydrocarbons**) are called **alkanes**. **Cycloalkanes** are alkanes in which the **carbon atoms** are arranged **in a ring**.

Unsaturated hydrocarbons contain carbon-carbon **double bonds** in **alkenes** and carbon-carbon **triple bonds** in **alkynes**.

Aromatic hydrocarbons contain a **benzene ring**. Benzene rings may be fused giving rise to **fused-ring aromatic hydrocarbons**.

2.2.1. Alkanes, cycloalkanes

The general formula for alkanes is: C_nH_{2n+2} ; for cycloalkanes C_nH_{2n} .

nomenclature

A set of rules for naming alkane derivatives is a part of the IUPAC system for organic compounds. The name is given by the longest chain, with **-ane** ending

isomerism

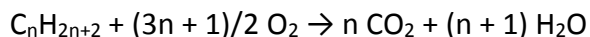
All the alkanes with 4 or more carbon atoms in them show **structural isomerism**. This means that there are two or more different structural formulae that you can draw for each molecular formula.

physical state and molecular structure, properties,

Methane, ethane, propane and butane are **gases** and used directly as fuels. Alkanes from pentane up to around $C_{17}H_{36}$ are **liquids**. Gasoline is a mixture of alkanes from pentane up to about decane. Kerosene contains alkanes from about $n=10$ to $n=16$. Above $n=17$ they are **solids** at room temperature.

chemical reactions

- Complete **combustion** (given sufficient oxygen) of any hydrocarbon produces carbon dioxide and water.

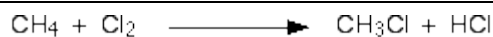


Incomplete combustion (where there isn't enough oxygen present) can lead to the formation of carbon or carbon monoxide.

-Chlorination of alkanes

There is no reaction in the dark. The interesting reactions happen in the presence of ultra-violet light (sunlight will do). These are **photochemical reactions**, and happen at room temperature.

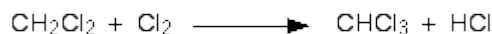
Substitution reactions happen in which hydrogen atoms in the methane are replaced one at a time by chlorine atoms.



chloromethane



dichloromethane



trichloromethane



tetrachloromethane

occurrence and use

Alkanes with higher values of n are found in diesel fuel, fuel oil, petroleum jelly, paraffin wax, motor oils, and for the highest values of n, asphalt.

Alkane derivatives are used in hundreds of products such as plastics, paints, drugs, cosmetics, detergents, insecticides, etc., so the fossil fuel resource from which we obtain the alkanes is much too valuable to burn it all as a motor fuel.

2.2.2. Alkenes (olefins)

Alkenes are hydrocarbons that ***contain the carbon-carbon double bond***.

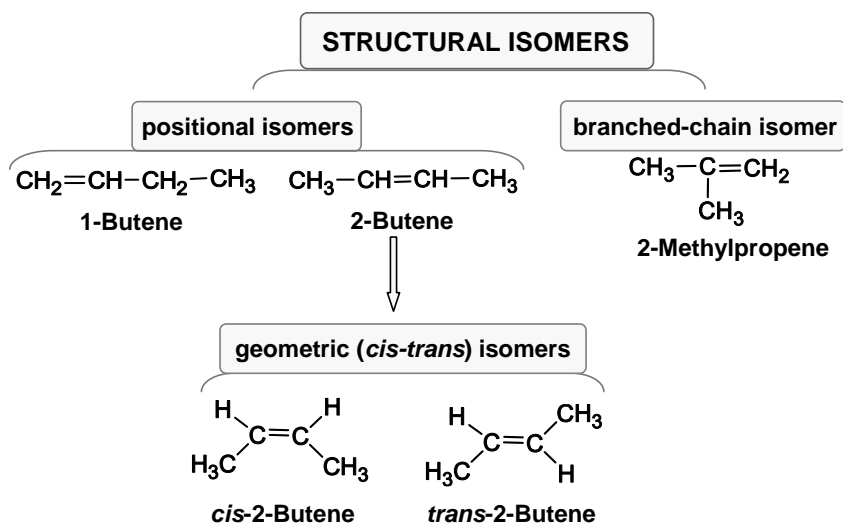
The ***double bond is a reactive site***, therefore it is assumed as a ***functional group***; and it is that primarily determines the properties of alkenes. ***Alkene*** molecules that contain only one double bond have the ***general formula, C_nH_{2n}***. They are, therefore, isomeric with cycloalkanes.

nomenclature

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes. Determine the base name by ***selecting the longest straight chain that contains the double bond*** and ***change the ending of the name of the alkane of identical length from ane to ene***.

isomerism

Examples can be given for structural and stereo isomers as it is shown by the isomers of butane:

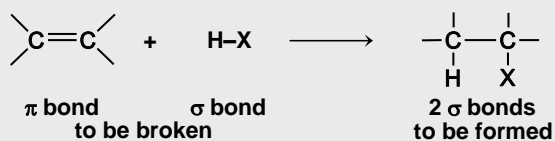


Structural and cis-trans (geometric) isomers of butene

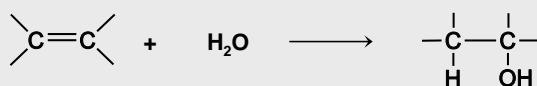
chemical reactions of the carbon-carbon double bond

The typical reaction of an alkene is addition reaction

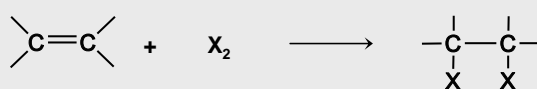
(a) Addition of hydrogenhalide (X= F, Cl, Br or I)



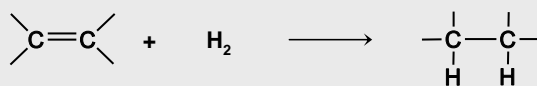
(b) Addition of water (hydration)



(c) Halogenation (X= F, Cl, Br or I)



(d) Hydrogenation (reduction)



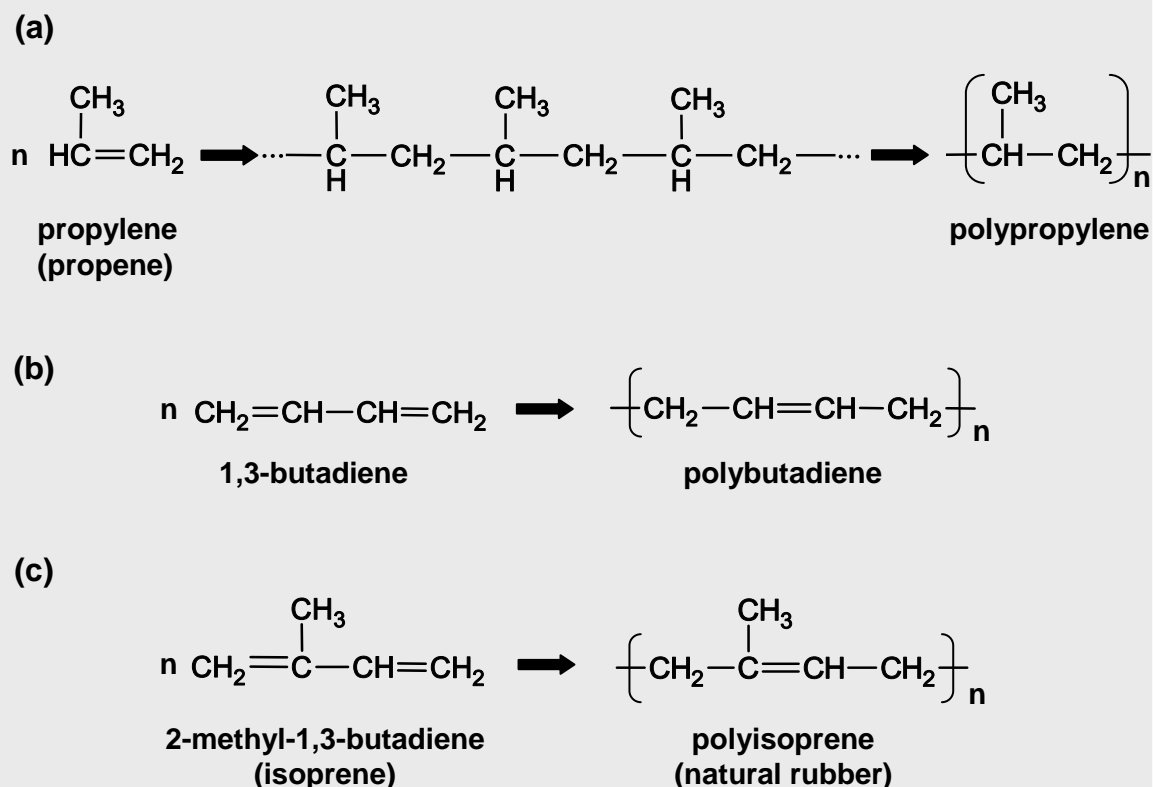
(e) Polymerization



Addition reactions of alkenes with various reactants

Hydrogenation reaction requires the presence of a catalyst to proceed with appropriate rate.

Under appropriate conditions, alkenes may even add to themselves to form chains of hundreds of carbon atoms. This giant molecule (macromolecule) of repeating units is called a **polymer** of the alkene. Because the polymer is formed by **linking molecules with multiple bonds** by an addition reaction, it is called an **addition polymer**.



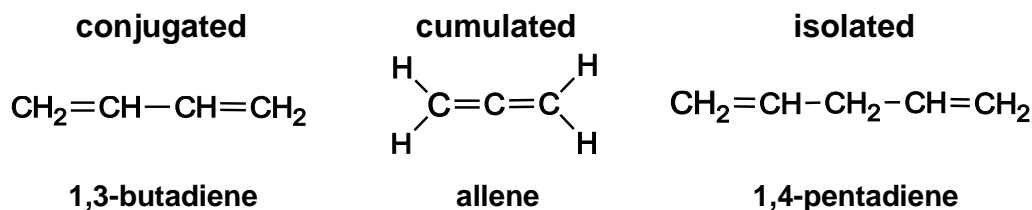
Polymerization of alkenes: formation of a polymer from propene (a); 1,3-butadiene (b); and from 2-methyl-1,3-butadiene called isoprene (c)

2.2.3 Hydrocarbons with multiple double bonds

Dienes

Dienes are alkenes that contain two carbon-carbon double bonds.

Dienes are named by the IUPAC system in **the same way as alkenes, except that the ending -diene is used, with two numbers to indicate the positions of the two double bonds**. This system is easily extended to compounds containing any number of double bonds.



Classification of distinct types of dienes

Conjugated dienes, too, undergo free-radical polymerization. From 1,3-butadiene the polymer differs from the polymers of simple alkenes in a very important way; each unit still contains one double bond. Natural rubber has a structure that strongly resembles these synthetic polydienes. It is a polymer of the conjugated diene, called 2-methyl-1,3-butadiene, or **isoprene**. The double bonds in the rubber molecule are important, since they provide reactive centers allowing **vulcanization of rubber**, the formation of **sulfur bridges between different chains**.

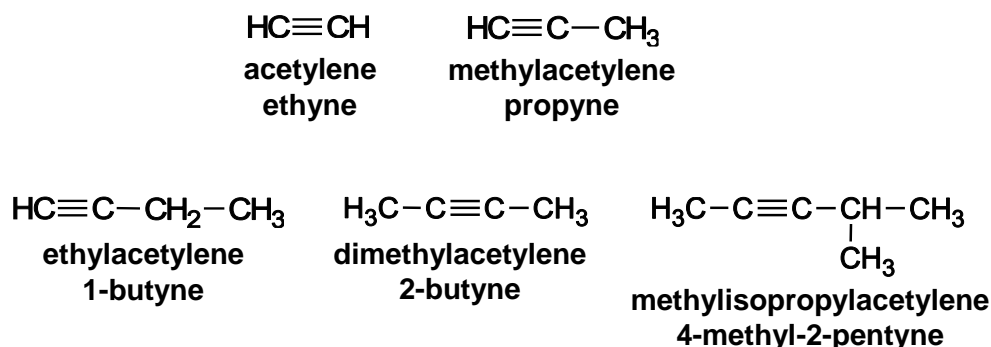
The **isoprene unit** is one of nature's favorite **building block**. It occurs in a wide variety of compounds isolated from plant and animal sources. For example, nearly all the **terpenes** (found in the essential oils of many plants) have carbon skeletons made up of joined isoprene units.

2.2.4 Alkynes

Alkynes are hydrocarbons that **contain the carbon-carbon triple bond**. The **general formula**, $\text{C}_n\text{H}_{2n-2}$.

nomenclature

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups.



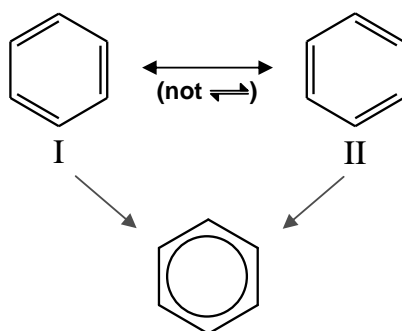
Structure and names for several alkynes

occurrence and use

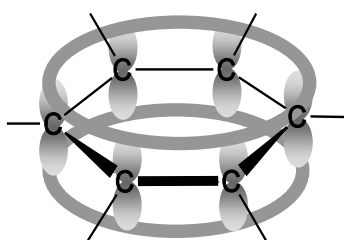
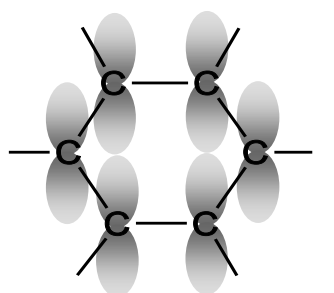
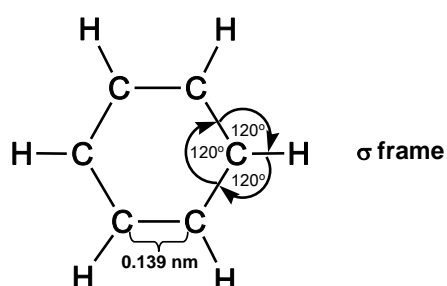
The alkyne of industrial importance is the simplest member of the family, **acetylene**. Enormous quantities of acetylene are consumed each year. It is sold to be used as a fuel for the oxyacetylene torch dissolved under pressure in acetone in tanks.

2.2.5 Aromatic hydrocarbons

The structure for benzene



Resonance structures for benzene and the structure of a “resonance hybrid”



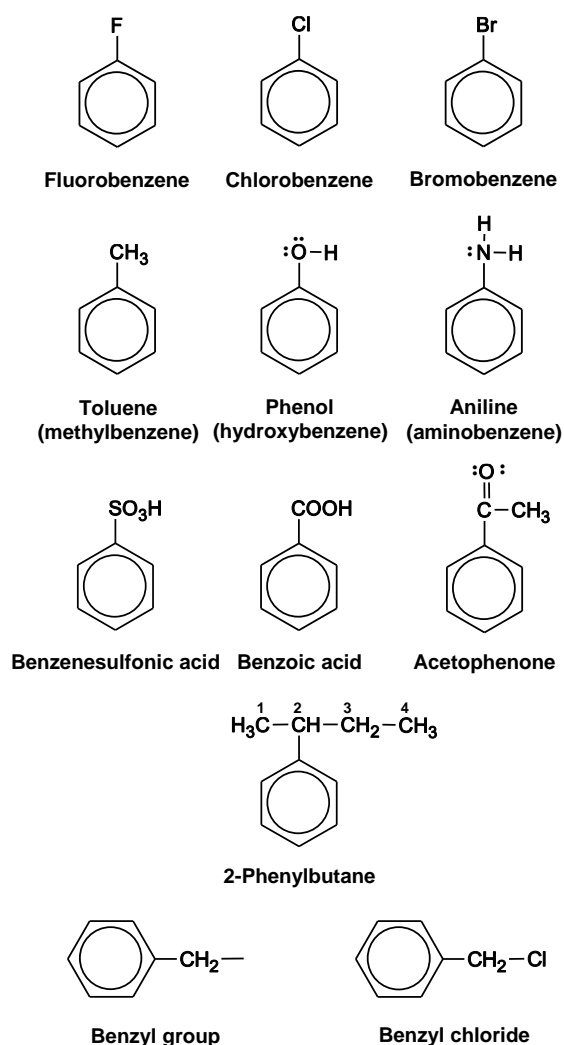
Hybridization of carbon atoms in benzene and overlap of the p electrons

Benzene is a symmetrical molecule in which the bond angles of the carbon atoms are 120° , constructing a planar six-membered ring from carbon atoms. All atoms, carbon and hydrogen atoms are lying in the same plane, σ -bonds are formed between the carbon

atoms and between the carbons and hydrogens, The remaining p orbitals of the carbons are perpendicular on this plane. The overlap of the orbitals (forming the π bonds) are not confined to specific double bonds (as it is indicated by Kekule formulas or by the resonance structures), rather the p orbitals overlap equally all around the ring. Benzene is stable because its six π electrons is spread equally along the ring and this electron delocalization is the source of the extra stabilization energy observed with aromatic compounds.

Hückel rule states that ***coplanar rings*** containing $(4n+2)$ π electrons, where $n=0, 1, 2, 3...$ etc., have closed shells of electrons like benzene, and should have substantial resonance or delocalization energies. In other words, ***6, 10, 14, 18, and 22, delocalized π electrons should be aromatic.***

Nomenclature and important representatives of benzene derivatives



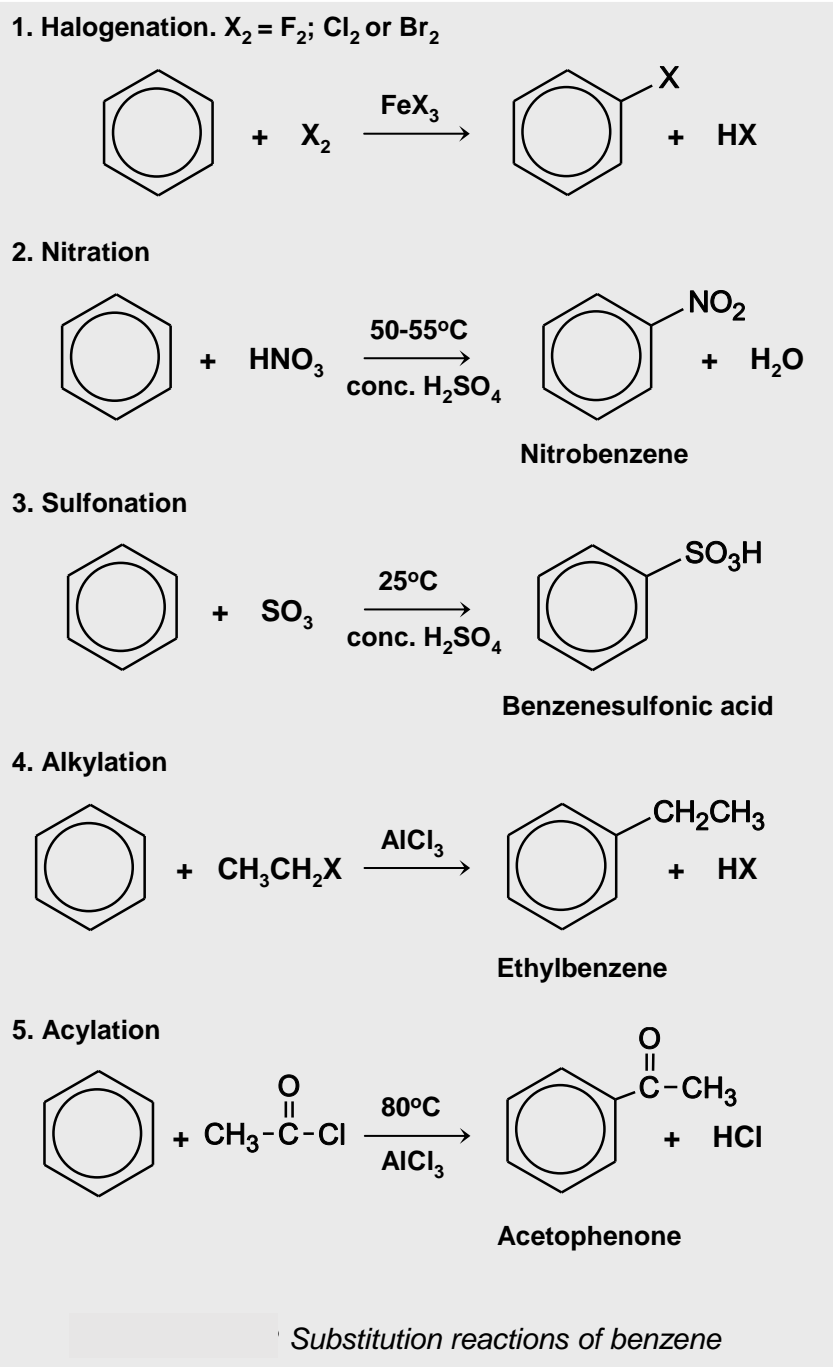
Nomenclature of monosubstituted benzenes

When two substituent are present, their relative positions are indicated by the use of ***ortho*** (1,2), ***meta*** (1,3) and ***para*** (1,4 positions), abbreviated ***o-***, ***m-***, and ***p-*** prefixes.

The benzene ring is numbered so as to give ***the lowest possible numbers to the substituents.***

Reactions of aromatic compounds

The most characteristic reactions of the aromatic compounds are the **substitution** reactions.



2.3 Halogenated organic compounds

Organic halogen compounds contain halogen atom covalently bonded to hydrocarbons. General formula R-X or Ar-X.

Most of the **organic halogen compounds** are **polar molecules**.

Because of dipole-dipole interactions the boiling points of alkyl halides are higher than the alkanes with similar molecular mass.

Reaction of alkyl halides: substitution reactions

2.4 Oxygen-containing organic compounds

2.4.1 Hydroxy compounds

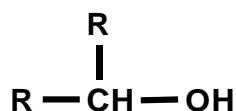
Alcohols are compounds in which a **hydroxyl group** is attached to a **saturated carbon**. Compounds that have a **hydroxyl group** attached **directly to a benzene ring** are called **phenols**.

Alcohols

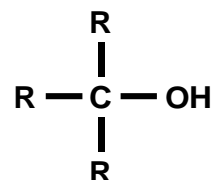
The saturated carbon to which the hydroxyl group is attached may be: (i) a carbon of a simple alkyl group: depending on the type of the carbon they could be **primary, secondary** and **tertiary** alcohols, whereas the number of the hydroxyl groups attached would give rise to **diols, triols...**



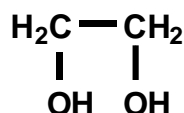
primary alcohol



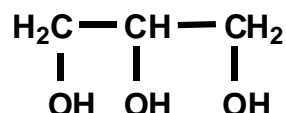
secondary alcohol



tertiary alcohol

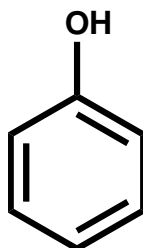


ethylene glycol
1,2-ethanediol



glycerol
1,2,3-propantriol

Phenol



2.4.2 Ethers

General structure **R-O-R**

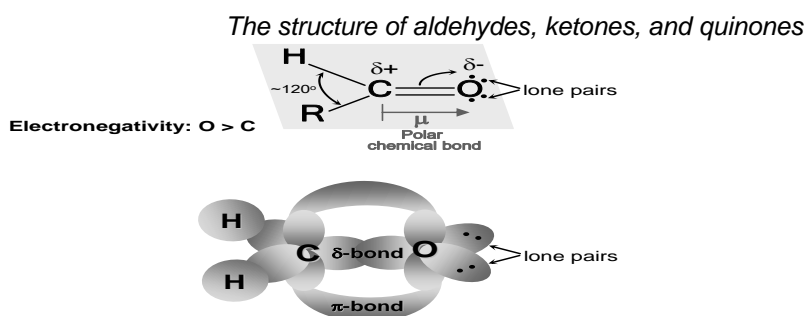
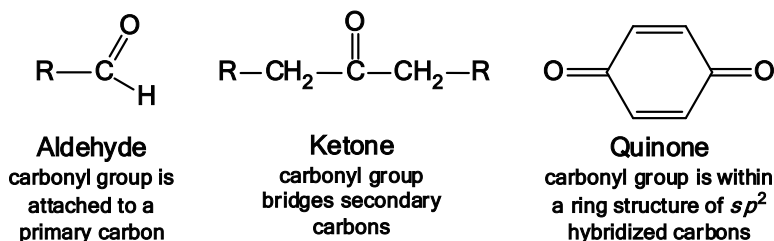
Important ethers with biological/medical significance

Diethyl ether ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$) is a colorless, inflammable liquid, it is extensively used as a solvent and was used as an **inhalation anesthetic** for years.

Thyroxine (the thyroid hormone) is a **naturally occurring diaryl ether**.

2.4.3 Oxo compounds

Aldehydes, ketones and quinones are organic compounds which **incorporate** a **carbonyl functional group, C=O**.



Nomenclature

IUPAC names of aldehydes have **-al** end;

ketones have **-one** end

Trivial name of some important aldehydes and ketones:

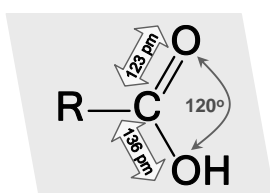
Formaldehyde, HCHO

Acetaldehyde, CH_3CHO

Aceton, CH_3COCH_3

2.4.4 Carboxylic acids and their salts

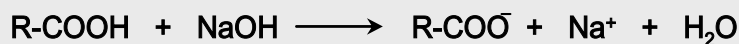
general formula for acids is **R-COOH**; R is $\text{C}_n\text{H}_{2n+1}$. The **functional group** of carboxylic acids is the **carboxyl group**



Carboxylic acids
salts

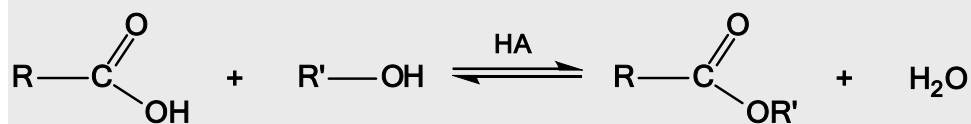
Figure 10.1 Structure of the carboxylic group

react with bases to form ionic



2.4.5 Esters

General formula: **R-COOR**

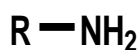


Preparation of ester from carboxylic acid and alcohol in an acid catalyzed equilibrium reaction

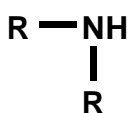
2.5 Nitrogen-containing organic compounds

2.5.1 Amines

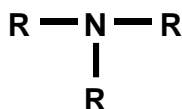
General structures of amines



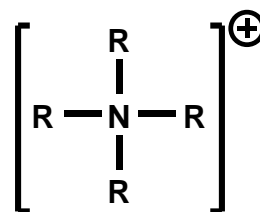
primary amine



secondary amine



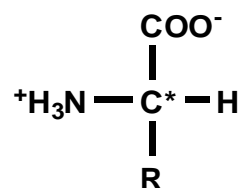
tertiary amine



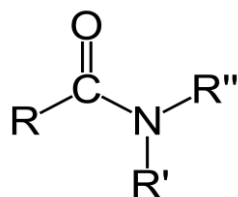
quaternary ammonium

2.5.2 Amino acids

structure of α -amino acid in zwitter ionic form



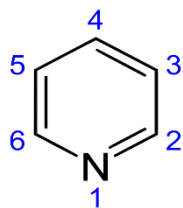
2.5.3 Amides



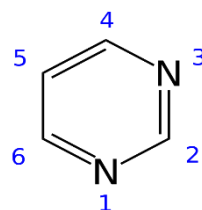
R = H or alkyl group

2.5.4 Heterocyclic aromatic compound

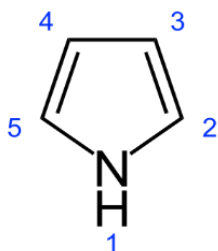
Pyridine



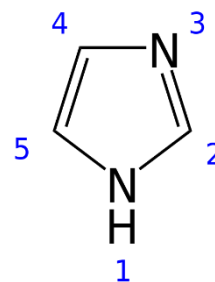
Pyrimidine



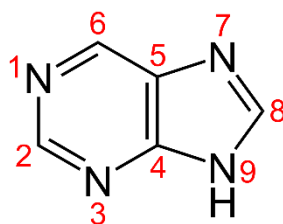
Pyrrole



Imidazol



Purin



Literature

Chemistry, 5th edition, 2008, J. E. McMurry and R. C. Fay, Pearson Education, Inc. Pearson Prentice Hall

Organic Chemistry for premedical students, F. Erdódi and C. Csontos, 2010, University of Debrecen, Medical and Health Science Center
