10. States of Matter : Gaseous and Liquid States

10.1 Introduction:

We have learnt that substances exist in one of the three main states of matter. The three distinct physical forms of a substance are Solid, Liquid, and Gas.

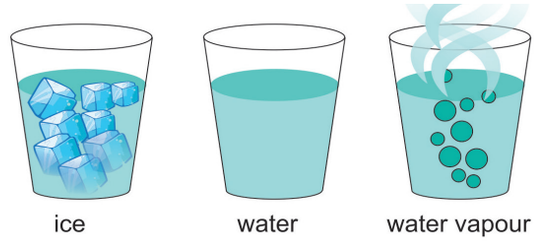


Fig. 10.1 : Different States of Water

Can you recall?

Water exists in the three different forms solid ice, liquid water and gaseous vapours.

Key points of differentiation between the three states can be understood as given in Table 10.1.

Three states of matter are interconvertible by exchange of Heat as given below:

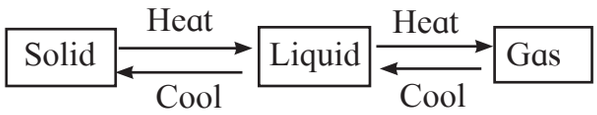
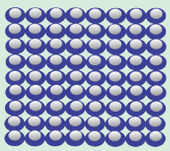
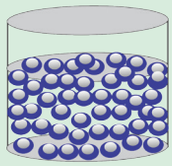
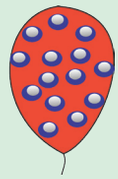


Table 10.1: Distinguishing points between Solid, Liquid and Gas

Sr. No.	Points	Solid	Liquid	Gas
1	Microscopic view Mean atomic/ molecular separation	 Mean separation ≈ 3-5A^0	 Mean separation ≈ 3-10A^0	 Mean separation > 5A^0
2	Arrangement of particles (atoms/ molecules)	Particles are tightly held, and have regular arrangement of atoms/ molecules	Particles are loosely packed, irregular arragement of particles	Particles are more loosely packed, highly irregular arrangement
3	Movement of particles	Particles cannot move freely as they occupy fixed positions.	Particles can move a small distance within the liquid	Particles are in continuous random motion.
4	Shape and volume	Has definite shape and volume	Takes the shape of the container and has definite volume.	Takes the shape and the volume of its container.
5	Intermoleculer space	Very small Intermolecular space	Moderate Intermolecular space	Large Intermolecular space.
6	Effect of a small change in temperature	Volume change is small	Moderate effect on volume change	Volume change significantly high.
7	Compression or Expansion	Practically Non- compressible	Small Compressibility	Compressible

10.2 Intermolecular Forces : Intermolecular forces are the attractive forces as well as repulsive forces present between the neighbouring molecules. The attractive force decreases with the increase in distance between the molecules. The intermolecular forces are strong in solids, less strong in liquids and very weak in gases. Thus, the three physical states of matter can be determined as per the strength of intermolecular forces.

The physical properties of matter such as melting point, boiling point, vapor pressure, viscosity, evaporation, surface tension and solubility can be studied with respect to the strength of attractive forces between the molecules. During the melting process intermolecular forces are partially overcome, whereas they are overcome completely during the vapourization process.

10.2.1 Types of Intermolecular Forces:

The four types of intermolecular forces are-

i. Dipole-dipole interactions
ii. Ion-dipole interactions
iii. Dipole-Induced dipole interaction
iv. London Dispersion Forces
v. Hydrogen bonding

i. Dipole-dipole interactions : Polar molecules experience dipole-dipole forces due to electrostatic interactions between dipoles on neighboring molecules.

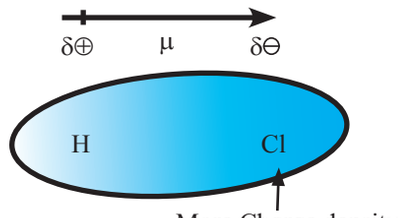
What are polar molecules or Polar covalent molecules? (Refer to Chapter 5).

Polar covalent molecule is also described as "dipole" meaning that the molecule has two 'poles'. The covalent bond becomes polar due to electronegativity difference between the bonding atoms. Hence polarity is observed in the compounds containing dissimilar atoms. For example, HCl molecule (see Fig. 10.2 (a)).

One end (pole) of the molecule has partial positive charge on hydrogen atom while at other end chlorine atom has partial negative charge (denoted by Greek letter 'δ' delta). As a result of polarisation, the molecule possesses the dipole moment.

Dipole moment (μ) is the product of the magnitude of the charge (Q) and the distance between the centres of positive and negative charge (r). It is designated by a Greek Letter (μ) (mu). Its unit is debye (D).

Dipole moment is a vector quantity and is depicted by a small arrow with tail in the positive centre and head pointing towards the negative centre.



Unequal sharing of electrons between the bonding atoms.

Fig 10.2 (a) : Polar molecule

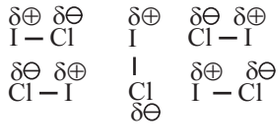


Fig 10.2 (b) : Dipole-dipole interaction

For example, the dipole moment of HF may be represented as: $\overset{\longrightarrow}{H\text{-}F}$:

The crossed arrow($\overset{\longrightarrow}{+\quad}$) above the Lewis structure represents an electron density shift.

Thus polar molecules have permanent dipole moments. When a polar molecule encounters another polar molecule, the positive end of one molecule is attracted to the negative end of another polar molecule. Many such molecules have dipoles and their interaction is termed as dipole-dipole interaction. These forces are generally weak, with energies of the order of 3-4 kJ mol^{-1} and are significant only when molecules are in close contact. i.e. in a solid or a liquid state.

For example C_4H_9Cl, (butyl chloride), CH_3 - O - CH_3 (dimethyl ether) ICl (iodine chloride B.P. 27 ^{0}C), are dipolar liquids. The molecular orientations due to dipole-dipole interaction in ICl liquid is shown in Fig. 10.2 (b).

In brief, more polar the substance, greater the strength of its dipole-dipole interactions. Table 10.2 enlists several substances with similar molecular masses but different dipole moments. From Table 10.2, it is clear that higher the dipole moment, stronger are the inter molecular forces, generally leading to higher boiling points.

Table 10.2 : Effect of dipole moments on boiling point (b.p.)

Substance	Molar Mass (amu)	Dipole Moment (D)	b.p. (K)
CH_3 - CH_2 - CH_3	44.10	0.1	231
CH_3 - O - CH_3	46.07	1.3	248
CH_3 - Cl	50.49	1.9	249
CH_3 - CN	41.05	3.9	355

When different substances coexist in single phase, following intermolecular interactions are present.

ii. Ion-dipole interactions : An ion-dipole force is the result of electrostatic interactions between an ion (cation or anion) and the partial charges on a polar molecule.

The strength of this interaction depends on the charge and size of an ion. It also depends on the magnitude of dipole moment and size of the molecule.

(Hydrated $Na^{\oplus}$ ion)

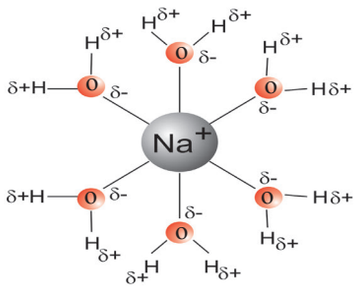


Fig. 10.2 (c) : $Na^{\oplus}$ ion(cation) - H_2O interaction

Ion-dipole forces are particularly important in aqueous solutions of ionic substances such as sodium chloride (NaCl). When an ionic compound, sodium chloride is dissolved in water, the ions get separated and surrounded by water molecules which is called **Hydration** of sodium ions.

Cations are smaller in size than the isoelectronic anions. The charge density on cation ($Na^{\oplus}$) is more concentrated than anion ($Cl^{\ominus}$). This makes the interaction between ($Na^{\oplus}$) and negative end of the polar H_2O molecule (Fig. 10.2 (c)) stronger than the corresponding interaction between ($Cl^{\ominus}$) and positive end of the polar H_2O molecule.

More the charge on cation, stronger is the ion-dipole interaction. For example, $Mg^{2\oplus}$ ion has higher charge and smaller ionic radius (78 pm) than $Na^{\oplus}$ ion (98 pm), hence $Mg^{2\oplus}$ ion is surrounded (hydrated) more strongly with water molecules and exerts strong ion-dipole interaction.

Thus the strength of interaction increases with increase in charge on cation and with decrease in ionic size or radius. Therefore, ion-dipole forces increase in the order :

$Na^{\oplus} < Mg^{2\oplus} < Al^{3\oplus}$.

iii. Dipole-Induced dipole interaction :

When polar molecules (like H_2O, NH_3) and nonpolar molecules (like benzene) approach each other, the polar molecules induce dipole in the non-polar molecules. Hence 'Temporary dipoles' are formed by shifting of electron clouds in nonpolar molecules. For example, Ammonia (NH_3) is polar and has permanent dipole moment while Benzene (C_6H_6) is non polar and has zero dipole moment. The force of attraction developed between the polar and nonpolar molecules is of the type dipole - induced dipole interaction. It can be seen in Fig 10.2(d) in the following manner:

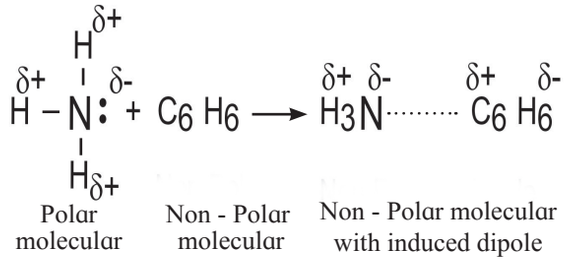


Fig. 10.2 (d) : Dipole - induced dipole interaction

iv. London Dispersion Force : The study of intermolecular forces present among nonpolar molecules or the individual atoms of a noble gas is very interesting. For example, Benzene (C_6H_6) has zero dipole moment and experiences no dipole-dipole forces, yet exists in liquid stage.

In case of nonpolar molecules and inert gases, only dipersion forces exist. Dispersion forces are also called as **London forces** due to an idea of momentary dipole which was proposed by the German Physicist, **Fritz London** in 1930. These forces are also called as **van der Waals forces**. It is the weakest intermolecular force that develops due to interaction between two nonpolar molecules. In general, all atoms and molecules experience London dispersion forces, which result from the motion of electrons. At any given instant of time, the electron distribution in an atom may be asymmetrical, giving the atom a short lived dipole moment. This momentary dipole on one atom can affect the electron distribution in the neighbouring atoms and induce momentary dipoles in them. As a result, weak attractive force develops.

For example, substances composed of molecules such as O_2, CO_2, N_2, halogens, methane gas, helium and other noble gases show van der Waals force of attraction.

The strength of London forces increases with increase in molecular size, molecular mass and number of electrons present in an atom or molecule.

When two nonpolar molecules approach each other, attractive and repulsive forces between their electrons and the nuclei will lead to distortions in the size of electron cloud, a property referred to as polarizability.

Polarizability is a measure of how easily an electron cloud of an atom is distorted by an applied electric field. It is the property of atom. The ability to form momentary dipoles that means the ability of another molecule to become polar by redistributing its electrons is known as **polarizability** of the atom or molecule.

More the number of electrons in a molecule, higher is its ability to become polar. Similarly more the spread out shapes, higher the dispersion forces present between the molecules. London dispersion forces are stronger in a long chain of atoms where molecules are not compact. This can affect physical property such as B.P. n-Pentane, for example boils at 309.4 K, whereas neo - pentane boils at 282.7 K. Here both the substances have the same molecular formula, C_5H_{12}, but n-pentane is longer and somewhat spread out, where as neo-pentane is more

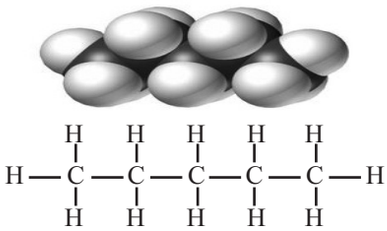


Fig 10.3 (a): Longer, less mpact molecule n-Pentane (b.p.= 309.4K)

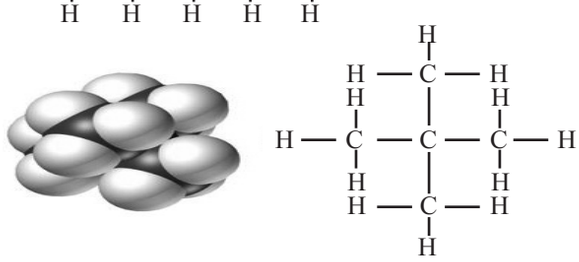


Fig 10.3 (b): More compact molecule neo - pentane (b.p.= 282.7K)

spherical and compact (see Fig. 10.3).

v. Hydrogen Bonding : A hydrogen bond is a special type of dipole-dipole attraction which occurs when a hydrogen atom is bonded to a strongly electronegative atom or an atom with a lone pair of electrons. Hydrogen bonds are generally stronger than usual dipole - dipole and dispersion forces, and weaker than true covalent or ionic bonds.

Definition : The electrostatic force of attraction between positively polarised hydrogen atom of one molecule and a highly electronegative atom (which may be negatively charged) of other molecule is called as **hydrogen bond**.

Strong electronegative atoms that form hydrogen bonds are nitrogen, oxygen, and fluorine. Hydrogen bond is denoted by (....) dotted line. Hydrogen bond which occurs within the same molecule represents **Intramolecular Hydrogen bond**.

A hydrogen bond present between two like or unlike molecules, represents **Intermolecular Hydrogen bond**.
(See Fig. 10.4 (a) and (b)).

i. Inter molecular H-bonding

H-bonding in H–F :

$H^{\delta+}–F^{\delta-}\cdots H^{\delta+}–F^{\delta-}\cdots H^{\delta+}–F^{\delta-}\cdots H^{\delta+}–F^{\delta-}$

H-bond

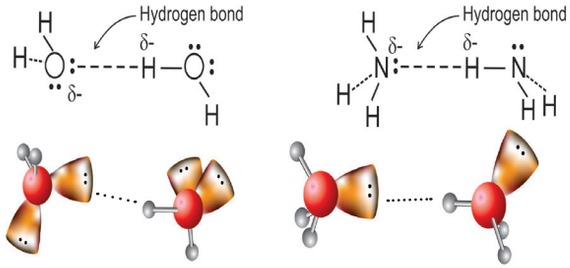
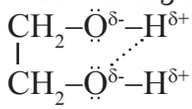


Fig. 10.4 : H-bonding in H_2O (above) and NH_3 (below) (solid line denotes covalent bond, dotted line denotes hydrogen bond)

ii. Intra molecular H-bonding :

H-bonding in ethylene glycol :



H - bonding and boiling point : Due to the presence of H-bonding in the compounds, more energy is required to break the bonds. Therefore, boiling point is more in case of liquid molecules containing H-bond. Hydrogen bonds can be quite strong with energies up to 40 kJ/mol.

Water in particular is able to form a vast three dimensional network of hydrogen bonds as shown in Fig. 10.5. It is because each H_2O molecule has two hydrogen atoms and two electron pairs on oxygen atom.

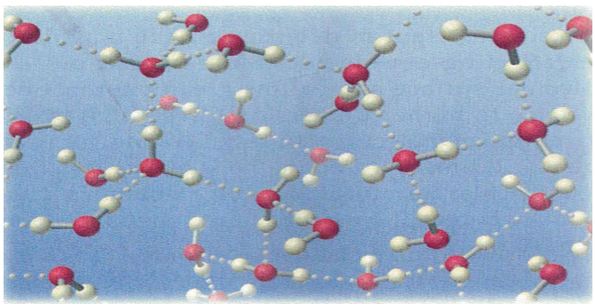


Fig. 10.5 : Liquid water contains a vast three dimensional network of hydrogen bonds

The boiling point generally increases with increase in molecular mass, but the hydrides of nitrogen (NH_3), oxygen (H_2O) and fluorine (HF) have abnormally high boiling points due to the presence of hydrogen bonding between the molecules.

Similarly due to presence of H- bond, viscosity of liquid increases. Hydrogen bonds play vital role in determining structure and properties of proteins and nucleic acid present in all living organisms. In case of gases intermolecular forces of attraction are very weak.

10.2.2 Intermolecular Forces and Thermal energy : Thermal energy is the origin of kinetic energy of the particles of matter that arises due to movement of particles (about which you must have learnt in Physics). It is directly proportional to the temperature; that means thermal energy increases with increase in temperature and vice versa.

Three states of matter are the consequence of a balance between the intermolecular forces of attraction and the thermal energy of the molecules.

If the intermolecular forces are very weak, molecules do not come together to make liquid or solid unless thermal energy is decreased by lowering the temperature.

When a substance is to be converted from its gaseous state to solid state, its thermal energy (or temperature) has to be reduced. At this stage, the intermolecular forces become more important than thermal energy of the particles.

Intermolecular Force Increases →

Gas → Liquid → Solid

Thermal energy decreases →

A comparison of various kinds of intermolecular forces discussed in this section is made in Table 10.3.

Table 10.3 : Comparison of Intermolecular Forces

Force	Strength	Characterstics
Ion-dipole	Moderate (10 - 50 kJ/mol)	Occurs between ions and polar solvents
Dipole-dipole	Weak (3 - 4 kJ/mol)	Occurs between polar molecules
London dispersion	Weak (1 - 10 kJ/mol)	Occurs between all molecules; strength depends on size, polarizability
Hydrogen bond	Moderate (10 - 40 kJ/mol)	Occurs between molecules with O-H, N-H, and H-F bonds

Can you tell?

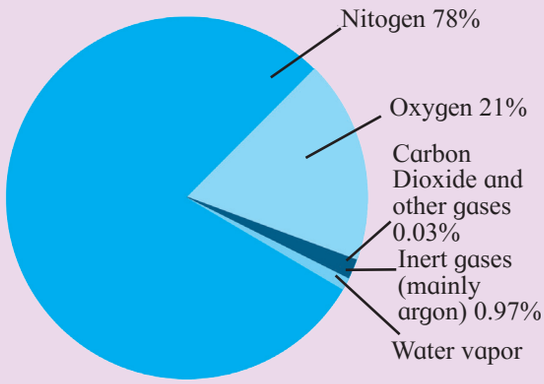
What are the various components present in the atmosphere?

Name five elements and five compounds those exist as gases at room temperature.

Just think

What is air?

It is a mixture of various gases. Air, we can not see but feel the cool breeze. The composition of air by volume is around 78 percent N_2, 21 percent O_2 and 1 percent other gases including CO_2. The chemistry of atmospheric gases is an important subject of study as it involves air pollution. O_2 in air is essential for survival of aerobic life.



Composition of air with respect to proportion of various gases

Do you know ?

Among the three compounds H_2, H_2S and H_2Se, the first one, H_2O has the smallest molecular mass. But it has the highest B.P. of 100^0C. B.P. of H_2S is -60^0C and of H_2Se is -41.25 ^{0}C. The extraordinary high B.P. of H_2O is due to very strong hydrogen bonding even though it has the lowest molecular mass.

10.3 Characteristic properties of Gases :

Under normal conditions, out of 118 elements from the periodic table, only a few (eleven) elements exist as gases. The gaseous state is characterized by the following physical properties :

1. Gases are lighter than solids and liquids i.e. possess lower density.
2. Gases do not possess a fixed volume and shape. They occupy entire space available and take the shape of the container.
3. Gas molecules are widely seperated and are in continuous, random motion. Therefore, gases exert pressure equally in all directions due to collision of gas molecules, on the walls of the container.
4. In case of gases, intermolecular forces are weakest.
5. Gases possess the property of diffusion which is a spontaneous homogenous inter mixing of two or more gases.
6. Gases are highly compressible.

Measurable properties of Gases : (Refer to Chapter 1) : Some Important measurable properties of the gases are given below :

1. Mass: The mass, m, of a gas sample is measure of the quantity of matter it contains. It can be measured experimentally. SI unit of mass of gas is kilogram (kg). 1kg = 10^3g.

The mass of a gas is realated to the number of moles (n) by the expression i.

i. $$n = \frac{\text{mass in grams}}{\text{molar mass in grams}} = \frac{m}{M}$$

The following expressions are also useful in calculations.

ii. $$n = \frac{\text{Number of molecules}}{\text{Avogadro Number}} = \frac{N}{N_A} = \frac{N}{6.022 \times 10^{23}}$$

iii. $$\text{n} = \frac{\text{Volume of a given gas in litres at STP}}{\text{22.414 litres at STP}}$$

2. Volume: Volume (V) of a sample of gas is the amount of space it occupies. It is expressed in terms of different units like Litres (L), mililitres(mL), cubic centimeter (cm^3), cubic meter (m^3) or decimeter cube (dm^3). SI Unit of the volume is cubic meter (m^3).

Most commonly used unit to measure the volume of the a gas is decimeter cube or litre.

1 L = 1000mL = 1000 cm^3 = 1dm^3

1 m^3 = 10^3 dm^3 = 10^3L = $10^6$$cm^3$ = 10^6 mL

3. Pressure: Pressure (P) is defined as force per unit area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{f}}{\text{a}}$$

Pressure of gas is measured with 'manometer' and atmospheric pressure is measured by 'barometer'.

SI Unit of pressure is pascal (Pa) or Newton per meter square (N m^{-2}).

1 Pa = 1 Nm^{-2} = 1 kg m^{-1} s^{-2}

1 bar = 1.00 × 10^5 Pa

The bar is now replacing the standard atmosphere (atm) as the most convenient unit of pressure.

1 atm = 76 cm of Hg = 760 mm of Hg = 760 torr as 1 torr = 1mm Hg

1 atm = 101.325 kPa = 101325 Pa = 1.01325 × 10^5 N m^{-2} = 1.01325 bar.

Can you tell?

What is the unit in which car-tyre pressure is measured ?

4. Temperature : It is the property of an object that determines direction in which energy will flow when that object is in contact with other object.

In scientific measurements temperature (T) is measured either on the celsius scale (^{0}C) or the Kelvin scale (K). (Note that degree sign is not used in Kelvin unit).

SI Unit of Temperature of a gas is kelvin (K). The celsius and kelvin scales are related by the expression

$$T\,\textbf{(K)} = \textbf{t}^0\,\textbf{C} + \textbf{273.15}$$

5. Density : It is the mass per unit volume.

$$d = \frac{m}{V}$$

∴ SI Unit of density is kg m^{-3}.

In the case of gases, relative density is measured with respect to hydrogen gas and is called vapour density.

$$\therefore \text{ Vapour density} = \frac{\text{molar mass}}{2}$$

6. Diffusion: In case of gases, Rate of diffusion of two or more gases is measured.

$$\text{Rate of diffusion} = \frac{\text{Volume of a gas diffused}}{\text{time required for diffusion}}$$

∴ SI Unit for Rate of diffusion is dm^3 s^{-1} or cm^3 s^{-1}

10.4 Gas Laws : The behavior of gases can be studied by four variables namely pressure, volume,temperature and the number of moles. These variables and measurable properties of the gases are related with one another through different gas laws.

Think of a gas in a cylinder or a sealed container. We can measure number of moles (n) of gas inside, the pressure (P) of a gas, the volume (V) of a gas (which is equal to the volume of the container) and the temperature (T) of the gas. The observed relationships between P, V, n and T are summarized by five gas laws: Boyle's law, Charles' law, Gay Lussac law, Avogadro law and Dalton's law.

The gas laws are based on the experimental observations made by the scientists. Further, these gas laws have played significant role in the development of chemistry.

10.4.1 Boyle's Law: (Pressure-Volume Relationship)

Do you know ?

How does the bicycle pump work ?
You can feel the increased pressure of a gas on your palm by pushing in the piston of a bicycle pump. As you push, you squash the same number of particles into a smaller volume. This squashing means particles hit the walls of the pump more often, increasing the pressure.

In 1662, Robert Boyle carried out large number of experiments on various gases. He observed that at constant temperature when the pressure was increased, the volume of the gas was reduced and vice versa.

Statement of Boyle's law: *For a fixed mass (number of moles 'n') of a gas at constant temperature, the pressure (P) of a gas is inversely proportional to the volume (V) of gas.*

OR

At constant temperature, the pressure of fixed amount (number of moles) of a gas varies inversely with its volume.

The law can be illustrated diagramatically as shown in Fig. 10.6

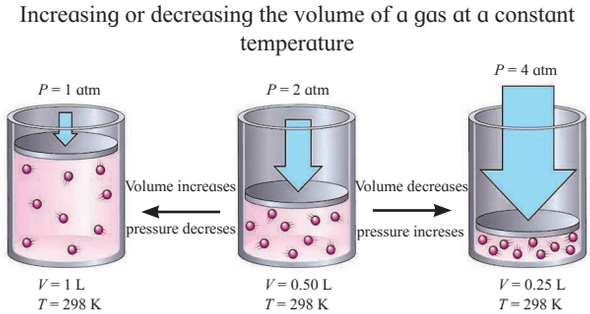


Fig. 10.6 : Schematic illustration of Boyle's Law

Mathematical Expression :

Mathematically, Boyle's law is expressed as

$$P \propto \frac{1}{V} \quad \text{(at constant T and n)}$$

$$\therefore P = k_1 \frac{1}{V} \quad \ldots\ldots\ldots\ldots \quad (10.1)$$

(where k_1 is proportionality constant)
on rearranging, Eq. (10.1) be comes :

$$\therefore P V = k_1 \quad \ldots\ldots\ldots\ldots \quad (10.2)$$

It means that at constant temperature, product of pressure and volume of the fixed amount of a gas is constant.

Thus, when a fixed amount of a gas at constant temperature (T) occuping volume V_1 initially at pressure (P_1) undergoes expansion or compression, volume of the gas changes to V_2 and pressure to P_2.

According to Boyle's law,

$$P_1V_1 = P_2V_2 = \text{constant} \quad \ldots\ldots(10.3)$$

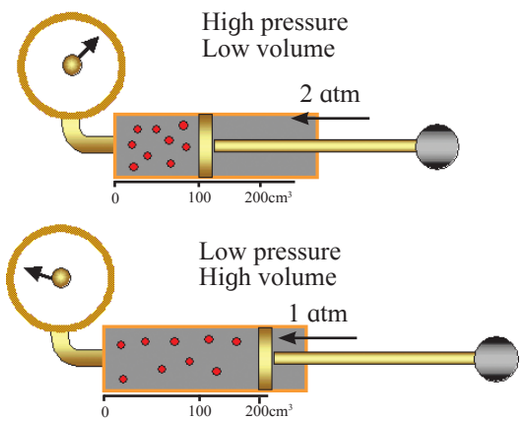
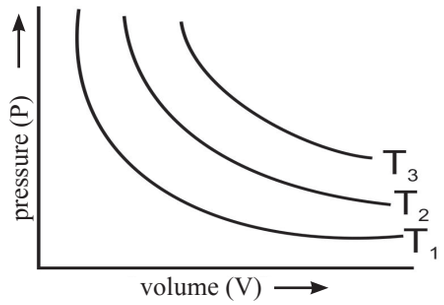


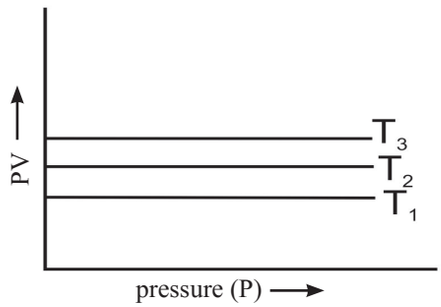
Fig. 10.7 : Schematic of the experiment Boyle's law

Figure 10.7 illustrates the Boyle's law experiment when the applied pressure increases from 1 atm to 2 atm and volume of the gas decreases from 200 cm^3 to 100 cm^3.

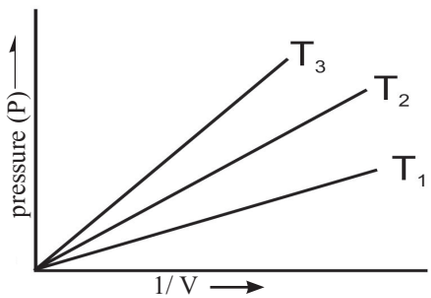
Graphical Representation : Figure 10.8 shows how the pressure-volume relationship can be expressed graphically. Figure 10.8 (a) shows a graph of the equation PV = k at a given constant temperature, known as Isotherm (constant temperature plot). For a given mass of a gas, the value of k varies only with temperature.



a. Graph of pressure, P, vs volume, V, of a gas at different temperatures T_1, T_2, T_3.



b. Graph of PV vs pressure, P, of a gas at different temperatures T_1, T_2, T_3.



c. Graph of pressure, P, of a gas vs 1/V at different temperatures T_1, T_2, T_3.

Fig. 10.8 : Boyle's law : Graphical representation

If the product of pressure and volume (PV) is plotted against pressure (P), a straight line is obtained paralled to x-axis (pressure axis) as in Fig 10.8 (b).

When the pressure (P) of the gas is plotted against ($1/V$), a straight line is obtained passing through the origin as shown in Fig. 10.8 (c), provided T and n are constant.

However, at high pressure, deviation from Boyle's law is observed in the behavior of gases.

Boyle's law in terms of density of gas : With increase in pressure, gas molecules get closer and the density (d) of the gas increases. Hence, at constant temperature, pressure is directly proportional to the density of a fixed mass of gas. Therefore, from Eq. (10.2).

$$PV = k_1 \qquad \text{.....(10.2)}$$

$$\therefore \quad V = \frac{k_1}{P} \qquad \text{.....(10.4)}$$

But $d = \frac{m}{V}$

On Substituting V from Eq. (10.4),

$$d = \left(\frac{m}{k_1}\right) \times P$$

$$\therefore d = k'P, \qquad \text{..... (10.5)}$$

where k' = New Constant.

$$\therefore \; \boldsymbol{d} \; \alpha \; \boldsymbol{P}$$

Above equation shows that at constant temperature, the pressure is directly proportional to the density of a fixed mass of the gas.

Internet my friend

- Watch Boyle's law experiment. www.socratica.youtube
- Find applications of Boyle's law.
- Try to study how Boyle's law helps in 'scuba-diving' i.e. Importance of Boyle's law in scuba-diving an exhilarating sport.

Problem: 10.1 : The volume occupied by a given mass of a gas at 298 K is 25 mL at 1 atmosphere pressure. Calculate the volume of the gas if pressure is increased to 1.25 atmosphere at constant temperature.

Given : $P_1 = 1$ atm, $V_1 = 25$ mL

$P_2 = 1.25$ atm, $V_2 = ?$

Solution :

According to Boyle's law,

$$P_1V_1 = P_2V_2$$

Substituting the values of P_1V_1 and P_2 in the above expression we get

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1 \times 25}{1.25} = 20 \text{ ml}$$

Volume occupied by the gas is 20 mL

10.4.2 Charles' law : (Temperature -Volume Relationship)

Just think

1. Why does bicycle tyre burst during summer?
2. Why do the hot air balloons fly high?

J. Charles (1746-1823) and Gay Lussac (1778-1850) worked independently on influence of temperature on volume of a gas. Their experiments showed that for a given mass of a gas at constant pressure its volume increases with an increase in temperature. It was found that for an increase of every degree of temperature, volume of the gas increases by $\frac{1}{273.15}$ of its original volume at 0 ^{0}C. This observation is expressed mathematically as follows :

$$V_t = V_0 + \frac{t}{273.15} V_0 \quad \ldots\ldots (10.6)$$

Where V_t and V_0 are the volumes of the given mass of gas at the temperatures t ^{0}C and 0 ^{0}C.

Rearranging the Eq. (10.6) gives

$$V_t = V_0 \left(1 + \frac{t}{273.15}\right)$$

$$\therefore V_t = V_0 \left(\frac{t + 273.15}{273.15}\right) \quad \ldots\ldots (10.7)$$

At this stage, a new scale of temperature was introduced, namely, the **absolute temperature scale**. This absolute temperature (T K) was defined as

T K = t ^{0}C + 273.15

This also called **thermodynamic scale of temperature**. The units of this absolute temperature scale is called (K) in the honour of **Lord Kelvin** who determined the accurate value of absolute zero as -273.15 ^{0}C in 1854. The Eq. (10.7) is now rewritten by replacing the celcius temperatures by absolute temperaturs as follows :

$$V_t = V_0 \left(\frac{T_t}{T_0}\right) \quad \ldots\ldots (10.8)$$

where $T_t = t + 273.15$ and $T_0 = 273.15$

The Eq. (10.8) on rearrangement takes the following form :

$$\frac{V_t}{T_t} = \frac{V_0}{T_0}$$

From this, a general equation can be written as follows :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \ldots\ldots (10.9)$$

$$\therefore \frac{V}{T} = \text{constant} = k_2$$

$$\therefore V = k_2 T \quad \ldots\ldots (10.10)$$

The Eq. (10.10) is the mathematical expression of Charles law, which is stated as follows :

'At constant pressure, the volume of a fixed mass of a gas is directly proportional to its temperature in kelvin.'

The law can be illustrated diagramatically as shown in Fig. 10.9.

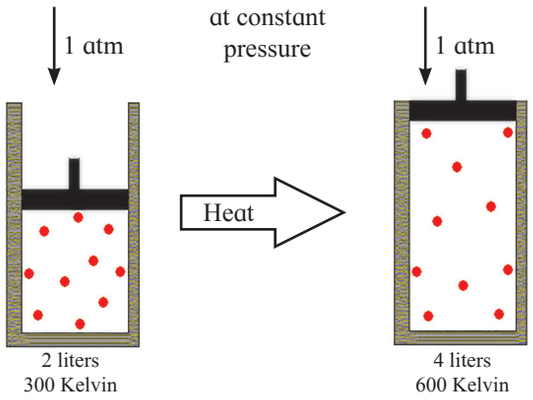


Fig. 10.9 : At constant pressure, volume changes with temperature

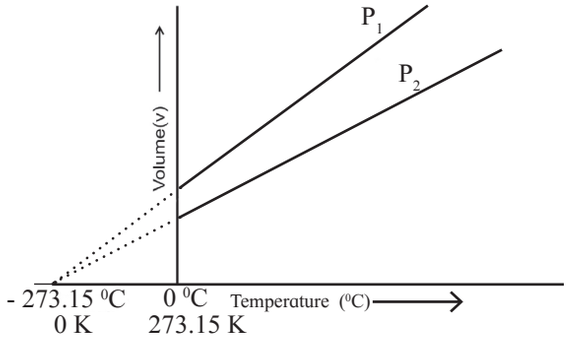


Fig. 10.10 : Graph of volume against temperature

Absolute zero temperature and Charles law

According to Charles law, Eq. (10.10), the graph of volume of a gas (at given constant pressure, say P_1) plotted versus its temperature in celsius, is a straight line with a positive slope. (See Fig. 10.10). On extending the line to zero volume, the line intercepts the temperature axis at -273.15 ^{0}C. At any other value of pressure, say P_2, a different straight line for the volume temperature plot is obtained, but we get the same zero - volume temperature intercept at - 273.15 ^{0}C. The straight line of the volume versus temperature graph at constant pressure is called **isobar**. Zero volume for a gas sample is a hypothetical state. In practice all the gases get liquified at a temperature higher than - 273.15 ^{0}C. This temperature is the lowest temperature that can be imagined but practically cannot be attained. It is the **absolute zero** temperature on the kelvin scale (0 K).

Isobars: A graph of volume (V) vs absolute temperature (T) at a constant pressure is known as Isobar.

Remember

On the kelvin scale, water freezes at at nearly 273 K and boils at about 373 K. (Note that we write kelvin temperatures in K without a ^{0}(degree) sign)

In short, Charles' law explains that at constant pressure, gases expand on heating and contract on cooling. Thus hot air is less dense than cold air.

10.4.3 Gay-Lussac's Law: (Pressure-Temperature Relationship) :

Just think

1. List out various real life examples of Charles law.
2. Refer and watch Charles law experiments.

Problem 10.2 : At 300 K a certain mass of a gas ocupies 1×10^{-4} dm^3 volume. Calculate its volume at 450 K and at the same pressure.

Given : $T_1 = 300$ K, $V_1 = 1 \times 10^{-4}$ dm^3, $T_2 = 450$ K, $V_2 = ?$

Solution : According to Charles' law, at constant pressure.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \therefore V_2 = \frac{V_1 \times T_2}{T_1}$$

$$= \frac{450 \times 1 \times 10^{-4}}{300}$$

$\therefore V_2 = 1.5 \times 10^{-4}$ dm^3

It relates the pressure and absolute temperature of a fixed mass of a gas at constant volume.

Statement: *At constant volume, pressure (P) of a fixed amount of a gas is directly proportional to its absolute temperature (T).*

Mathematical Expression:

Mathematically, the law can be expressed as :

$P \propto T$

$\therefore P = k_3 T$ .....(10.11)

$\therefore \frac{P}{T}$ = constant (at constant V and m)

Graphical Representation : When a graph is plotted between pressure (P) in atm and Temperature (T) in kelvin, a straight line is obtained as shown in Fig. 10.11. It is known as **isochore**. With the help of this law, one can unterstand relation between pressure and temperature in day to day life.

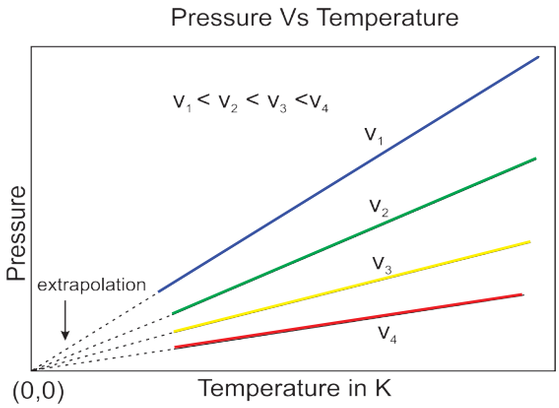


Fig. 10.11 : Pressure Vs Temperature graph of a gas

10.4.4 Avogadro Law: (Volume-Amount Relationship) :

Use your brain power

Why the pressure in the automobile tyres changes during hot summer or winter season?

In 1811 Italian scientist Amedeo Avogadro combined Dalton's atomic theory with Gay Lussac's Law of combining volumes (Chapter 1) to put forth what is known as **Avogadro law**. It states that **equal volumes of all gases at the same temperature and pressure contain equal number of molecules**. This means that at a fixed temperature and pressure, the volume of a gas depends upon the number of molecules of the gas, that is, the amount of the gas.

Avogadro law can be expressed mathematically as : $V \propto n$ (where 'n' is the number of moles of the gas in volume 'V')

On converting the proportionality into equation we get

$$V = k_4 n \quad \text{..... (10.12)}$$

or $\frac{V}{n}$ = constant (at constant temperature and pressure)

Avogadro Law can be well represented from Fig. 10.12 as follows :

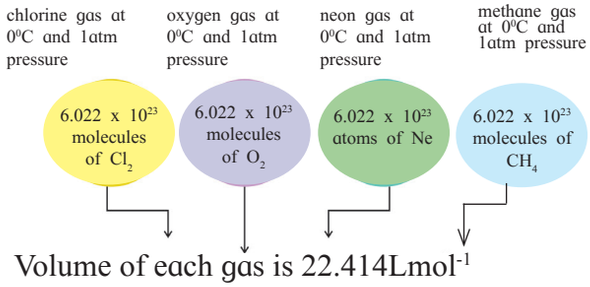


Fig. 10.12 : Avogadro Law

Can you recall?

1 mole of a gas contains Avogadro number of molecules = 6.022×10^{23}.

As the volume of a gas is directly proportional to number of moles, one mole of any gas at STP occupies 22.414 $Lmol^{-1}$ volume. This volume is known as **molar volume**.

Remember

What are STP conditions?

STP means Standard Temperature and Pressure.

IUPAC has set STP as

standard Pressure = **1 bar = 10^5 Pa**

standard temperature = **273.15 K = 0°C**

Under these STP conditions molar volume of an ideal gas or mixture of two or more gases = **22.71 L mol^{-1}**

The old STP conditions are also in use, where

standard pressure = **1 atm = 1.013 bar**

standard temperature = **273.15 K = 0°C**

Under the old STP conditions molar volume of an ideal gas or mixture of two or more gases = **22.414 L mol^{-1}**

Relation between molar mass and density (d) of a gas : We have learnt how to find number of moles of a gas. (Refer to Chapter 1.)

We know,

$$n = \frac{m}{M},$$

where m = mass of a gas,

M = molar mass of a gas.

Substituting in equation (10.12) we get,

$$V = k_4 \times \frac{m}{M}$$

$$\therefore M = k_4 \frac{m}{V} \quad \text{..... (10.13)}$$

But $\frac{m}{V} = d$

substituting this in Eq. (10.13) we get

$$\boldsymbol{M = k_4 d} \quad \text{..... (10.14)}$$

Where d = density of a gas.

M = Molar mass

m = mass of gas

$\therefore d \propto M$

From Eq. (10.14), we can conclude that the density of a gas is directly proportional to its molar volume.

10.5 Ideal Gas Equation : A gas that follows strictly all the three laws; Boyle's law, Charles' law and Avogadro law is an **ideal gas**. Practically an ideal gas does not exist. Real gases show ideal behaviour under certain specific condition, when intermolecular interactions are practically absent. Yet these three gas laws and the ideal gas equation obtained by treating them mathematically are found to be very valuable in Chemistry.

10.5.1 Derivation of Ideal Gas Equation :

The three gas laws, namely, Boyle's law, Charles law and Avogadro law, are combined mathematically to obtained what is called ideal gas equation.

Let us write the propotionalities of the three gas laws :

1. At constant T and n, $V \propto \frac{1}{P}$ (Boyle's law)
2. At constant P and n, $V \propto T$ (Charles' law)
3. At constant P and T, $V \propto n$ (Avogadro law)

Combining all the above three mathematical propornalities we get,

$$V \propto \frac{nT}{P}$$

Converting this proportionality into an equation by introducing a constant of proportionality we get,

$$\therefore V = R\left(\frac{nT}{P}\right)$$

On rearraninging above equation, we obtain,

$$\therefore \boldsymbol{PV = nRT} \quad \text{..... (10.15)}$$

This equation is known as the **Ideal Gas Equation**. In the ideal gas equation, if three variables are known, fourth can be calculated. It describes the state of an ideal gas, therefore, it is also called as equation of state. Here **R** is called **Gas constant**, The value of R is the same for all the gases. Therefore it is called Universal gas constant.

10.5.2 Values of 'R' in different Units :

The value of R depends upon the units used to express P, V and T. Hence we recall STP conditions for determining values of 'R'.

i. R in SI Unit (in Joules) : Value of R can be calculated by using the SI units of P,V and T. Pressure P is measured in N m^{-2} or Pa, volume V in meter cube (m^3) and Temperature T in kelvin (K),

$$R = \frac{PV}{nT}$$

$$\therefore R = \frac{10^5 \text{Pa} \times 22.71 \times 10^{-3}\ \text{m}^3}{1\ \text{mol} \times 273.15\ \text{K}}$$

$$\therefore R = 8.314\ \text{Pa m}^3\ \text{K}^{-1}\ \text{mol}^{-1}$$

then $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

ii. R in litre atmosphere : If pressure (P) is expressed in atmosphere (atm) and volume in litre (L) or decimeter cube (dm^3) and Temperature in kelvin (K), (that is, **old STP conditions**), then value of R is :

$$R = \frac{1\text{atm} \times 22.414\ \text{L}}{1\ \text{mol} \times 273.15\ \text{K}}$$

$$\therefore R = 0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1}$$

OR

$$R = 0.08206\ \text{dm}^3\ \text{atm K}^{-1}\text{mol}^{-1}$$

Note : Often Pressure (P) is measured in atmosphere (atm). The conversion between the units is done by noting that 1 atm = 1.013×10^5 Nm^{-2} or 1 atm = 101.3 kPa

Table 10.4 Unit of R

Pressere (P)	Volume (V)	Number of moles (n)	Temperture (T)	Gas consant (R)
Pa (pascals)	m^3	mol	K	8.314 J K^{-1} mol^{-1}
atm	dm^3	mol	K	0.0821 atm dm^3 K^{-1} mol^{-1}
atm	L	mol	K	0.0821 L atm K^{-1} mol^{-1}

iii. R in calories:

We know, 1 calorie = 4.184 Joules

$$\therefore R = \frac{8.314}{4.184} = 1.987 \cong 2 \text{ cal } K^{-1} \text{ mol}^{-1}$$

While using ideal gas equation one should use consistent units. The most common units are shown in Table 10.4.

10.5.3 Expression for Molar mass :

Ideal gas equation can be used to determine the Molar mass (M) of a compound. Rearranging the equation (10.15)

$$n = \frac{PV}{RT} \quad \text{.....} \quad (10.16)$$

But for a known mass of a gas 'm', the number of moles,

$$n = \frac{m}{M}$$

On substituting this in equation (10.16) we get

$$\frac{m}{M} = \frac{PV}{RT}$$

$$\therefore M = \frac{mRT}{PV} \quad \text{.....} \quad (10.17)$$

10.5.4 Combined Gas law :

The ideal gas equation is written as

$$PV = nRT \quad \text{.....} \quad (10.15)$$

On rearranging Eq. (10.15) we get

$$\therefore \frac{PV}{T} = nR = \text{constant}$$

$$\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{.....} \quad (10.18)$$

The ideal gas equation used in this form is called **combined gas law**. We have to assume a gas under two different sets of conditions where pressure, volume and temperatures are written for one state as P_1, V_1, T_1 and the other state as P_2, V_2, T_2, respectively.

Problem 10.3 : A sample of N_2 gas was placed in a flexible 9.0 L container at 300K at a pressure of 1.5 atm. The gas was compressed to a volume of 3.0L and heat was added until the temperature reached 600K. What is the new pressure inside the container?

Given Data : $V_1 = 9$ L $V_2 = 3$L
$P_1 = 1.5$ atm $T_2 = 600$K
$T_1 = 300$ k $P_2 = ?$

Solution : According to combined gas law equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \therefore \frac{1.5 \times 9}{300} = \frac{P_2 \times 3}{600}$$

$\therefore P_2 = 9$ atm

Problem 10.4 : Find the temperature in ^{0}C at which volume and pressure of 1 mol of nitrogen gas becomes 10 dm^3 and 2.46 atmosphere respectively.

Given : P = 2.46 atm, V = 10 dm^3, n = 1mol, R = 0.0821 dm^3-atm$k^{-1}$$mol^{-1}$
T = ?

Solution : Ideal gas equation is

$$PV = nRT$$

$$\therefore T = \frac{PV}{nR} = \frac{2.46 \times 10}{1 \times 0.0821}$$

T = 299.63K

Temp. in ^{0}C = 299.63 - 273.15
= 26.48 ^{0}C

10.5.4 Relation between density, molar mass and pressure :

Ideal gas equation can be expressed in terms of density as follows :

$$PV = nRT \quad \text{.....} \quad (10.5)$$

On rearranging it gives

$$\frac{n}{V} = \frac{P}{RT}$$

But we know $n = \frac{m}{M}$

On substituting value of 'n', rearranged equation becomes-

$$\therefore \frac{m}{MV} = \frac{P}{RT} \quad \text{(at constant temperature)}$$

$$\therefore \frac{d}{M} = \frac{P}{RT} \quad \text{..... (10.19)}$$

where $\frac{m}{V} = d$ = density of a gas

On rearranging equation (10.19) we get expression to calculate molar mass of a gas in terms of its density.

$$M = \frac{dRT}{P} \quad \text{.....(10.20)}$$

From equation (10.19) ***Boyle's law*** *can be stated in terms of density as : at constant temperature, pressure of a given mass of gas is directly proportional to its density.*

10.5.6 Dalton's law of Partial Pressure :

John Dalton not only put forth the atomic theory, but also made several contributions to understanding of the behaviour of gases. He formulated the law of partial pressure in 1801. This law is applicable for those gases which do not react chemically on mixing. The pressure exerted by an individual gas in a mixture of two or more gases is called **partial pressure**. It is also the pressure that each gas would exert if it were present alone. Daltons law of partial pressure is stated as :

The total pressure of a mixture of two or more non reactive gases is the sum of the partial pressures of the individual gases in the mixture.

Mathematically, Dalton's law may be expressed as,

$$P_{Total} = P_1 + P_2 + P_3 + \text{.... (at constant } V \text{ and } T)$$

Where P_{Total} is the total pressure of the mixture and P_1, P_2, P_3, ... are the partial pressures of the individual gases 1, 2, 3, ... in the mixture.

Partial pressure and mol fraction : We know that the pressure of a pure gas is given by the ideal gas equation

$$P = \frac{nRT}{V} \quad \text{.... (10.21) } (V \text{ and } T \text{ are constant})$$

$$\therefore P \propto n.$$

Consequently, the pressure of an individual gas in a mixture of gases is proportional to its amount in that mixture. This implies that the total pressure (P_T) of a mixture of gases at constant volume (V) and Temperature (T) is equal to the sum of the pressure that individual gas exerts in the mixture. This is Dalton's law of partial pressures. It is shown in Fig. 10.13.

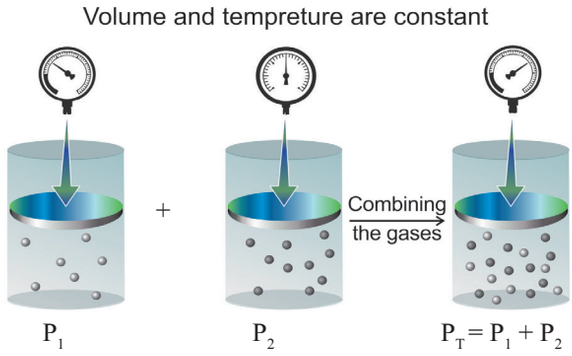


Fig. 10.13 : Schematic illustration of Dalton's law of partial pressures

Just think

Do all pure gases obey all the gas laws? Do the mixtures of gases obey the gas laws ? Yes, the gas laws are also applicable to the mixtures of gases. As we have learnt in section 10.5.3 that the measurable properties of mixture of the gases such as pressure, temperature, volume and amount of gaseous mixture are all related by an ideal gas law.

The partial pressures of individual gases can be written in terms of ideal gas equation as follows :

$$P_1 = n_1\left(\frac{RT}{V}\right), \quad P_2 = n_2\left(\frac{RT}{V}\right),$$

$$P_3 = n_3\left(\frac{RT}{V}\right), \text{ ... and so on .... (10.21)}$$

$$\therefore P_{Total} = n_1\left(\frac{RT}{V}\right) + n_2\left(\frac{RT}{V}\right) + n_3\left(\frac{RT}{V}\right) \text{.....}$$

$$= \left(\frac{RT}{V}\right)(n_1 + n_2 + n_3...) = \frac{RT}{V} n_{Total}$$

..... (10.22)

Mole fraction of any individual gas in the mixture is given by the equation

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3...} = \frac{n_1}{n_{Total}} \quad .. (10.23)$$

From Eq. (10.21) and Eq. (10.23) we get

$$n_1 = P_1 \Big/ \left(\frac{RT}{V}\right) \quad .... (10.24)$$

and

$$n_{Total} = P_{Total} \Big/ \left(\frac{RT}{V}\right) \quad .... (10.25)$$

By combining equation Eq. (10.24) and Eq. (10.25) we get

$$\frac{n_1}{n_{Total}} = X_1 = \frac{P_1 \Big/ \left(\frac{RT}{V}\right)}{P_{Total} \Big/ \left(\frac{RT}{V}\right)} = \frac{P_1}{P_{Total}}$$

..... (10.26)

Therefore it follows that

$$P_1 = X_1 . P_{Total} \quad ..... (10.27)$$

Similarly,

$P_2 = X_2 . P_{Total}$, $P_3 = X_3 . P_{Total}$ and so on.

Thus partial pressure of a gas is obtained by multiplying the total pressure of mixture by mole fraction of that gas.

Just think

Where is the Dalton's law applicable? The most important gas mixture is of course the air around us. Dalton law is useful for the study of various phenomena in air including air pollution.

Aqueous Tension : A vapor is a gas in contact with a liquid of the same substance. For example, the 'gas' above the surface of liquid water is described as water vapour. The pressure of the water vapour is known as its **vapour pressure**.

Suppose the liquid water is placed into a container and air above is pumped away and the container is sealed. Then the liquid water evaporates and only water vapour remains in the above space. After sealing, the vapour pressure increases initially, then slows down as some water molecules condense back to form liquid water. After a few minutes, the vapour pressure reaches a maximum called the **saturated vapour pressure**. (We will learn more about in section 10.9.2) The pressure exerted by saturated water vapour is called **Aqueous Tension (P_{aq}).**

Problem 10.5 : A mixture of 28g N_2, 8 g He and 40 g Ne has 20 bar pressure. What is the partial pressure of each of these gases ?

Solution : Partial pressure mole fraction x total pressure

Step 1 : Determine the number of moles (n) of each gas from its mass (m) and molar mass (M), using the formula

$$n = \frac{m}{M}$$

$$n_{N_2} = \frac{28\ g}{28\ g\ mol^{-1}} = 1\ mol$$

$$n_{He} = \frac{8\ g}{4\ g mol^{-1}} = 2\ mol$$

$$n_{Ne} = \frac{40g}{28\ g\ mol^{-1}} = 2\ mol$$

Step 2 : Determine the mole fraction of each gas using the formula

$$x_{N_2} = \frac{n}{n_{Total}}$$

$$x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{He} + n_{Ne}} = \frac{1\ mol}{(1 + 2 + 2)\ mol} = \frac{1}{5}$$

$$x_{He} = \frac{n_{He}}{n_{Total}} = \frac{2\ mol}{5\ mol} = \frac{2}{5}$$

Similarly $X_{Ne} = \frac{2}{5}$

Step 3 : Calculate the partial pressure

$$P_{N_2} = X \times P_{Total} = \frac{1}{5} \times 20\ bar = 4\ bar$$

$$P_{He} = X_{He} \times P_{Total} = \frac{2}{5} \times 20\ bar = 8\ bar$$

$$P_{Ne} = X_{Ne} \times P_{Total} = \frac{2}{5} \times 20\ bar = 8\ bar$$

When a gas is collected over water in a closed container, it gets mixed with the saturated water vapour in that space. The measured pressure, therefore, corresponds to the pressure of the mixture of that gas and the saturated water vapour in that space.

Pressure of pure and dry gas can be calculated by using the aqueous tension. It is obtained by subtracting the aqueous tention from total pressure of moist gas.

$$\therefore P_{Dry\ gas} = P_{Total} - P_{aq}$$

i.e. $P_{Dry\ gas}$ = P_{Total} - Aqueous Tension

Table 10.5 : Aqueous Tension of Water (Vapour Pressure) as a function of Temperature

Temp. (K)	Pressure (bar)	Temp. (K)	Pressure (bar)
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

The above table reflects that Aqueous Tension increases with increase in temperature.

10.6 Kinetic Molecular Theory of Gases :

The kinetic molecular theory of gases is a theoretical model put forth to explain the behavior of gases.

Assumptions of kinetic molecular theory of gases :

1. Gases consist of tiny particles (molecules or atoms).
2. On an average, gas molecules remain far apart from each other. Therefore the actual volume of the gas particles is negligible as compared to the volume of the container. (That is why the gases are highly compressible).
3. The attractive forces between the gas molecules are negligible at ordinary temperature and pressure. (As a result gas expands to occupy entire volume of the container).
4. Gas molecules are in constant random motion and move in all possible directions in straight lines. They collide with each other and with the walls of the container.
5. Pressure of the gas is due to the collision of gas particles with the walls of container.
6. The collisions of the gas molecules are perfectly elastic in nature, which means that the total energy of the gaseous particle remains unchanged after collision.
7. The different molecules of a gas move with different velocities at any instant and hence have different kinetic energies. But average kinetic energy of the gas molecules is directly proportional to the absolute temperature.
   Average K.E. $\propto$ T

10.7 Deviation from Ideal behaviour : An **ideal gas** is the one that exactly follows the ideal gas equation. On rearranging the ideal gas equation, n = PV/RT. If we use 1 mole of any gas then the ratio PV/RT is predicted to have numerical value of 1 at all pressures. If a gas does not obey the ideal gas law, the ratio will be either greater than 1 or less than 1, such a gas is said to be a **Real Gas**.

A. Ideal Gas:

1. A gas that obeys all the gas laws over the entire range of temperature and pressure.
2. There are no ineractive forces between the molecules.
3. The molecular volume is negligibly small compared to the volume occupied by the gas. These are point particles.

B. Real Gas :

1. Real gas does not obey Boyle's law and Charles' law under all the conditions of temperature and pressure.

A deviation from the ideal behaviour is observed a **high pressure and low temperature** It is due to two reasons.

(1) The intermolecular attractive forces are not negligible in real gases. These do not allow the molecules to collide the container wall with full impact. This results in decrease in the pressure.

(2) At high pressure, the molecular are very close to each other. The short range repulsive forces start operating and the molecules behave as small but hard spherical particles.

The volume of the molecule is not negligible. Therefore,x less volume is available for molecular motion.

At very low temperature, the molecular motion becomes slow and the molecules are attracted to each other due to the attractive force. Hence, here again the behaviour of the real gas deviates from the ideal gas behaviour.

Deviation with respect to pressure can be studied by plotting pressure (P) vs volume (V) curve at a given temperature. (See Fig. 10.14 and Table 10.6).

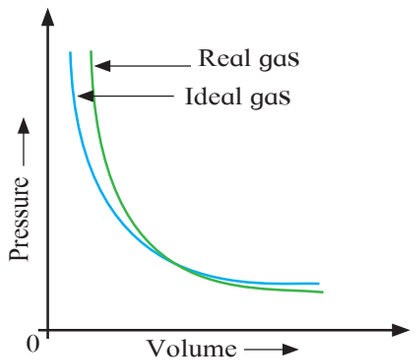


Fig. 10.14 : Plot of pressure Vs volume for real and ideal Gas

At very high pressure, the measured volume is more than theoretically calculated volume assuming ideal behaviour. But at low pressure, measured and calculated volumes approach each other.

Compressibility Factor (Z) : Real Gases show ideal behavior when pressure approaches zero. Deviation from ideal behaviour can be measured in terms of compressibility factor Z which is the ratio of product PV and nRT.

$$Z = \frac{PV}{nRT}$$

Figure 10.15 shows the graph of Z vs P. It is a straight line parallel to x - axis (pressure axis) where $Z = 1$.

For ideal gas $Z = 1$ at all the value of temperature and pressure. The significance of Z is better understood from the following derivation. we can write two equation (10.28) and (10.29) for real and ideal gas respectively.

$$Z = \frac{PV_{real}}{nRT} \quad \text{..... (10.28)}$$

$$\text{and} \quad 1 = \frac{PV_{ideal}}{nRT} \quad \text{..... (10.29)}$$

$$\therefore \quad \frac{P}{nRT} = \frac{I}{V_{ideal}}$$

Substituing the value of $\frac{P}{nRT}$ in Eq. (10.28), we get

$$Z = \frac{V_{real}}{V_{ideal}} \quad \text{..... (10.30)}$$

Table 10.6 : Difference between Ideal Gas and Real Gas

Ideal gas	Real Gas
1. Strictly obeys Boyle's and Charles' law. $\frac{PV}{nRT} = 1$	1. Shows deviation from Boyle's and Charles' law at high pressure and temperature. i.e. obeys Boyle's law and Charles' law at low pressure and high temperature. $\frac{PV}{nRT} \neq 1$
2. Molecules are perfectly elastic.	2. Molecules are not perfectly elastic.
3. No attraction or repulsion between the gas molecules i.e. collision without loss of kinetic energy (K.E.)	3. Intermoleculer attraction is present, hence collision takes place with loss of kinetic energy.
4. Actual volume of the gas molecules is negligible as compared to total volume of the gas.	4. Actual volume of individual gas molecule is significant at high pressure and low temperature.
5. Can not liquify even at low temperature but continues to obey Charles' law and finally occupies zero volume at -273^{0}C.	5. Undergo liquefaction at low temperature when cooled and compressed.
6. Such a gas does not exist.	6. Gases that exist in nature like H_2, O_2, CO_2 N_2, He, etc.

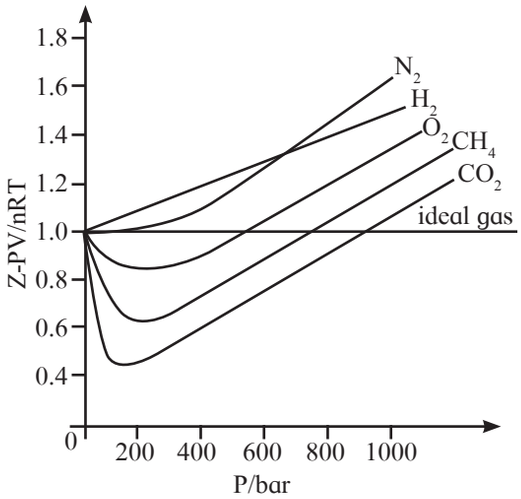


Fig. 10.15 : Graph of compressibility factor Z versus pressure for some gases

The Eq.(10.30) implies that the compressibility factor is the ratio of actual molar volume of a gas to its molar volume if it behaved ideally, at that temperature and pressure.

A positive deviation in Z, (Z > 1), means that the volume of a molecule cannot be neglected and the gas is difficult to compress. **At lower pressure**, the gases have Z = 1 or Z < 1. Under this conditon the molecular volume is negligible and the gases are compressible. Here, the gases show ideal behaviour.

10.7 Liquefaction of gases and critical constant : Most gases behave like ideal gases at high temperature. For example, the PV curve of CO_2 gas at 50^0C is like the ideal Boyle's law curve. As the temperature is lowered the PV curve shows a deviation from the ideal Boyle's law curve. At a particular value of low temperature the gas gets liquified at certain increased value of pressure. For example, CO_2 gas liquifies at 30.98 ^{0}C and 73 atmosphere pressure (See Fig. 10.16).

This is the highest temperature at which liquid CO_2 can exist. Above this temperature, howsoever large the pressure may be, liquid CO_2 cannot form. Other gases also show similar behaviour.

The temperature above which a substance cannot be liquified by increasing pressure is called its critical temperature (T_c).

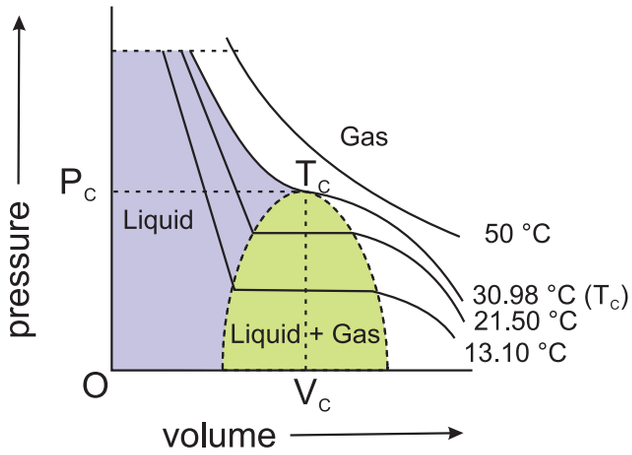


Fig. 10.16 : Liquefaction of CO_2 : Isotherms at various temperature

Above the critical temperature a substance exists only as gas. **The molar volume at critical temperature is called the critical volume (V_c)**. and **the pressure at the critical temperature is calles the critical pressure (P_c)** of that substance. The Table 10.7 gives the values of these three critical constants for some common gases.

Table 10.7 : Critical constants for common Gases

Substance	Tc / K	Pc/ bar	Vc/dm^{3}mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

From the Table 10.7 it is seen that the gases that we come across in everyday life, namely, N_2 and O_2 , have T_c values much below 0 ^{0}C and their P_c values are high. Consequently, liquefaction of O_2 and N_2 (and air) requires compression and cooling.

The T_c value of CO_2 nearly equals the room temperature, however, its P_c value is very high. Therefore CO_2 exists as gas under ordinary condition.

Problem 10.5 : Water has T_c = 647.1 K and P_c = 220.6 bar. What do these values imply about the state of water under ordinary conditions?

Solution : The T_c and P_c values of water are very high compared to the room temperature and common atmosheric pressure. Consequently water exists in liquid state under ordinary condition of temperature and pressure.

Study of PV curves of various gases at different temperatures reveals that under certain conditions the substance changes completely from gaseous to liquid state or liquid to gaseous state, without having the coexistence of two states. In other words, there is a continuity between the gaseous and liquid state. This continuity is recognized by using the term **Fluid** for either gas or liquid. Under these conditions liquid is just a very dense gas. Liquid and gas can be distingushed from each other only when the fluid is at a temperature below T_c.

Remember

When a liquid, which is exposed to atmosphere, is heated, its vapour pressure increases. Eventually it becomes equal to the atmospheric pressure. At this temperature the vaporisation takes place throughout the bulk of the liquid, and the vapour formed escapes freely, into the surroundings. We call this **boiling point** of the liquid. The boiling temperature (boiling point) depends upon the pressure to which the surface of the liquid is exposed. If the pressure is **1 atm**, the boiling temperature is called **normal boiling point**. If the pressure is **1 bar**, the boiling temperature is called **stadard boiling point**.

For water: normal b.p. = 100 ^{0}C, standard b.p. = 99.6 ^{0}C

Problem 10.6

CO_2 has T_c = 38.98^{0}C and P_c = 73 atm. How many phases of CO_2 coexist at (i) 50 ^{0}C and 73 atm, (ii) 20 ^{0}C and 50 atm.

Solution:

(i) 50 ^{0}C and 73 atm represent a condition for CO_2 above its T_c. Therefore, under this condition CO_2 exists only as single phase.

(ii) 20^0 C and 50 atm represent a condition for CO_2 below its T_c. Therefore, under this condition two phases of CO_2, namely, liquid and gas can coexist

Problem 10.7 : In which of the following cases water will have the highest and the lowest boiling point ?

Water is boiled

a. in an open vessel,

b. in a pressure cooker,

c. in a evacuated vessel.

Solution : Higher the pressure to which a liquid is exposed, higher will be its boiling point. The pressure to which water is exposed is maximum in the pressure cooker and minimum in the evacuated vessel. Therefore b.p. of water is highest in (b) and lowest in (c).

Internet my friend

1. https://chem.libretexts.org>bookshelves. Gas laws : overview
2. Collect information about State of Mater

10.8 Liquid state : Liquid state is the intermediate state between solid state and gaseous state. Molecules of liquid are held together by moderately strong intermolecular forces and can move about within the boundary of the liquid. As a result, liquid posseses properties such as fluidity, definite volume and ability to take shape of the bottom of the container in which it is placed. Different liquids are characterized by their quantitative properties such as density, boiling point, freezing point, vapour pressure, surface tension and viscosity. We will look at some of these propeties in the following sections.

10.8.1 : Vapour Pressure : Molecules of liquid have a tendency to escape from its surface to form vapour about it. This called evaporation. When a liquid is placed in a closed container.It undergoes evaporation and vapours formed undergo condensation. At equilibrium, the rate of evaporation and rate of condensation are equal. The pressure exerted by the vapour in equilibrium with the liquid is known as **saturated vapour pressure** or simply **vapour pressure**.

The vapour pressure of water is also called **Aqueous Tension**. (Refer to Table 10.5) Schematically vapour pressure is explained in Fig. 10.17.

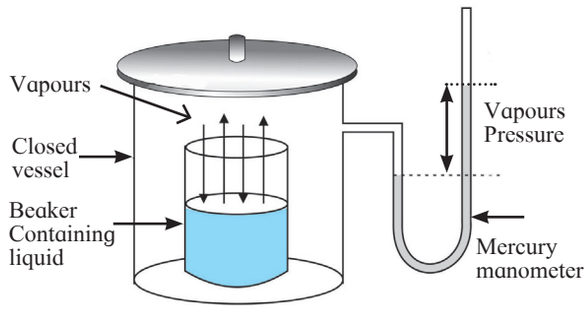


Fig. 10.17 : Vapour pressure of a liquid

Factors affecting vapour pressure :

a. Nature of liquid : Liquids having relatively weak intermolecular forces possess high vapour pressure. These are called valatile liquids. For example, petrol evaporates quickly than motor oil.

b. Temperature : When the liquid is gradually heated, its temperature rises and its vapour pressure increases.

Unit : Vapour pressure is measured by means of a manometer. The most common unit for vapour pressure is torr. 1 torr = 1 mm Hg. For example, water has a vapour pressure of apporximately 20 torr at room temperature. (Refer to section 10.5.6 and Table 10.5)

Just think

What makes the oil rise through the wick in an oil lamp ?

10.8.2 Surface Tension : Many phenomena such capillary rise of liquids, spherical shapes of liquid drops are due to the property of liquids called **surface tension**. Surface of a liquid acts as a stretched membrane. The particles in the bulk of liquid are uniformly attracted in all directions and the net force acting on the molecules present inside the bulk is zero. But the molecules at the surface experience a net attractive force towards the interior of the liquid, or the forces acting on the molecules on the surface are imbalanced (see Fig.10.18). Therefore, liquids have a tendency to minimize their surface area.

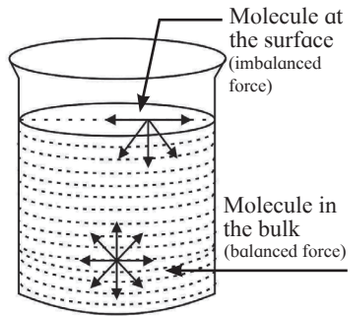


Fig. 10.18 : Imbalance of forces at the surface of a liquid

Surface tension is a temperature dependent property. When attractive forces are large, surface tension is large. Surface tension decreases as the temperature increases. With increase in temperature, kinetic energy of molecules increases. So intermolecular forces of attraction decrease, and thereby surface tension decreases.

The force acting per unit length perpendicular to the line drawn on the surface of liquid is called surface tension.

Unit : Surface tension is measured in SI Unit, Nm^{-1}, denoted by Greek letter "γ" (Gamma)

Application of surface tension :

i. Cleaning action of soap and detergent is due to the lowering of interfacial tension between water and oily substances. Due to lower surface tension, the soap solution penetrates into the fibre, surrounds the oily substance and washes it away.

ii. Efficacy of toothpastes, mouth washes and nasal drops is partly due to presence of substances having lower surface tension. This increases the efficiency of their penetrating action.

10.8.3 Viscosity : As noted earlier, liquids (fluids) have a tendency to flow. Viscosity measures the magnitude of internal friction in a liquid or fluid to flow as measured by the force per unit area resisting uniform flow, different layers of a liquid flow with different velocity. This called **laminar flow**. Here, the layers of molecules in the immediate contact of the fixed surface remains stationary. The subsequent layers slip over one another. Strong intermolecular forces obstruct the layers from slipping over one another, resulting in a friction between the layers.

Viscosity is the force of friction between the successive layers of a flowing liquid. It is also the resistance to the flow of a liquid.

When a liquid flows through a tube, the central layer has the highest velocity, whereas the layer along the inner wall in the tube remains stationary. This is a result of the viscosity of a liquid (see Fig. 10.19). Hence, a velocity gradient exists across the cross-section of the pipe/tube.

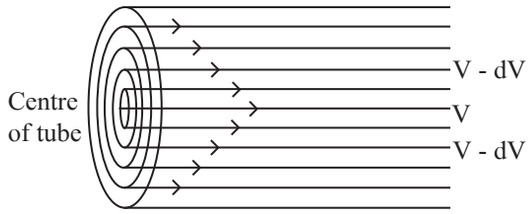


Fig. 10.19 : Laminar flow of a liquid (fluid) through a tube/pipe

Viscosity is a temperature dependent property.

$$\text{Viscosity } \alpha \frac{1}{\text{Temperature}}$$

Viscosity also depends on molecular size and shape. Larger molecules have more viscosity and spherical molecules offer the least resistance to flow and therefore are less viscous. Greater the viscosity, slower is the liquid flow.

Unit : Viscosity is expressed in terms of **coefficient of viscosity, 'η' (Eta)**. It is defined as the degree to which a fluid resists flow under an applied force, measured by the tangential frictional force per unit area per unit velocity gradient when the flow is laminar.

SI unit of viscosity coefficient is **N s m^{-2}** (newton second per square meter). In CGS system the unit (η) is measured in poise.

1 poise = 1 gm cm^{-1}s^{-1} = 10^{-1} kg m^{-1}s^{-1}

Illustration of viscosity :

i. Lubricating oils are viscous liquids. Gradation of lubricating oils is done on the basis of viscosity. A good quality Lubricating oil does not change its viscosity with increase or decrease in temeperature.

ii. Increase blood viscosity than the normal value is taken as an indication of cardio vascular disease.

iii. Glass panes of old buildings are found to become thicker with time near the bottom. This is one evidence which indicates that glass is not a solid but a supercooled viscous liquid.

Internet my friend

https://www.britannica.com/science/viscosity.

Exercises

1. Select and write the most appropriate alternatives from the given choices.

A. The unit of viscosity is
   a. dynes b. newton
   c. gram d. poise

B. Which of the following is true for 2 moles of an ideal gas ?
   a. PV = nRT b. PV = RT
   c. PV = 2RT d. PV = T

C. Intermolecular forces in liquid are -
   a. greater than gases
   b. less than solids
   c. both a and b
   d. greater than solids

D. Interactive forces are ..... in ideal gas.
   a. nil b. small
   c. large d. same as that of real gases

E. At constant temperature the pressure of 22.4 dm^3 volume of an ideal gas was increased from 105 kPa to 210 kPa, New volume could be-
   a. 44.8 dm^3 b. 11.2dm^3
   c. 22.4 dm^3 d. 5.6dm^3

2. Answer in one sentence.

A. Name the term used for mixing of different gases by random molecular motion and ferquent collision.

B. The pressure that each individual gas would exert if it were alone in the container, what do we call it as ?

C. When a gas is heated the particles move more quickly. What is the change in volume of a heated gas if the pressure is kept constant ?

D. A bubble of methane gas rises from the bottom of the North sea. What will happen to the size of the bubble as it rises to the surface ?

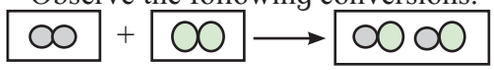
E. Convert the following temperatures from degree celcius to kelvin.
   a. -15° C b. 25° C
   c. -197° C d. 273° C

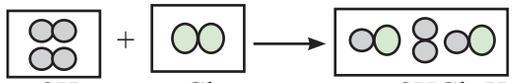
F. Convert the following pressure values into Pascals.
   a. 10 atmosphere c 107000 Nm^{-2}
   b. 1 kPa. d. 1 atmosphere

G. Convert :
   a. Exactly 1.5 atm to pascals
   b. 89 kPa to newton per square metre (Nm^{-2})
   c. 101.325 kPa to bar
   d. -100° C to kelvin
   e. 0.124 torr to standard atmosphere

H. If density of a gas is measured at constant temperature and pressure then which of the following statement is correct ?
   a. Density is directly proportional to molar mass of the gas.
   b. Greater the density greater is the molar mass of the gas.
   c. If density, temperature and pressure is given ideal gas equation can be used to find molar mass.
   d. All the above statements are correct.

I. Observe the following conversions.

a. 

b. 

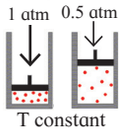
Which of the above reactions is in accordance with the priciple of stoichiometry ?

J. Hot air balloons float in air because of the low density of the air inside the balloon. Explain this with the help of an appropriate gas law.

3. Answer the following questions.

A. Identify the gas laws from the following diagrams.

Diagrams | Gas laws

a. 

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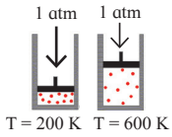
b. 

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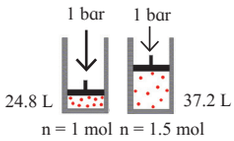
c. 

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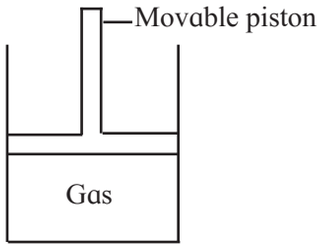
B. Consider a sample of a gas in a cylinder with a movable piston.



Show digramatically the changes in the position of piston, if -

a. Pressure is increased from 1.0 bar to 2.0 bar at constant temperature.

b. Temperature is decreased from 300 K to 150 K at constant pressure

c. Temperature is decreased from 400 K to 300 K and pressure is decreased from 4 bar to 3 bar.

D. List the characteristic physical properties of the gases.

E. Define the terms: a. Polarizability
b. Hydrogen bond
c. Aqueous tension
d. Dipole moment

F. Would it be easier to drink water with a straw on the top of the Mount Everest or at the base ? Explain.

G. Identify type of the intermolecular forces in the following compounds.

a. CH_3 - OH b. $CH_2 = CH_2$
c. $CHCl_3$ d. CH_2Cl_2

H. Name the types of intermolecular forces present in Ar, Cl_2, CCl_4 and HNO_3

I. Match the pairs of the following :

'A'	'B'
a. Boyle's law	i. at constant pressure and volume
b. Charles' law	ii. at constant temperature
	iii. at constant pressure

J. Write the statement for :
(a) Boyle's law (b) Charles' law

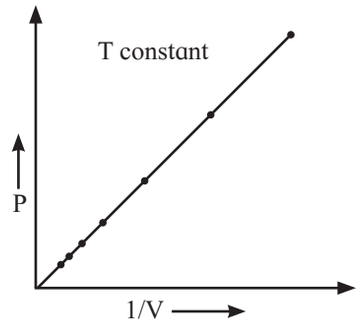
K. Differentiate between Real gas and Ideal gas.

4. Answer the following questions

A. State and write mathematical expression for Dalton's law of partial pressure and explain it with suitable example.

B. Derive an Ideal gas equation. Mention the terms involved in it. Also write how it is utilised to obtain combined gas law.

C. With the help of graph answer the following -



At constant temperature,

a. Graph shows relation between pressure and volume. Represent the relation mathematically.

b. Identify the law.

c. Write the statement of law.

D. Write Postulates of kinetic theory of gases.

E. Write a short note on -

a. Vapour pressure.

b. Surface tension

c. Viscosity.

5. Solve the following

A. A balloon is inflated with helium gas at room temperature of 25^{0}C and at 1 bar pressure when its initial volume is 2.27L and allowed to rise in air.

As it rises in the air external pressure decreases and the volume of the gas increases till finally it bursts when external pressure is 0.3bar. What is the limit at which volume of the balloon can stay inflated ? (Ans:7.567L)

B. A syringe has a volume of 10.0 cm^3 at pressure 1 atm. If you plug the end so that no gas can escape and push the plunger down, what must be the final volume to change the pressure to 3.5 atm?

(Ans:2.9 cm^3)

C. The volume of a given mass of a gas at 0^0C is 2 dm^3. Calculate the new volume of the gas at constant pressure when

a. The temperature is increased by 10^0C.

(Ans: 2.07 dm^3)

b.The temperature is decreased by10^0C.

(Ans:1.93 dm^3)

D. A hot air balloon has a volume of 2800 m^3 at 99^0 C. What is the volume if the air cools to 80^0 C?

(Ans:2657 m^3)

E. At 0^0C, a gas occupies 22.4 liters. How nuch hot must be the gas in celsius and in kelvin to reach volume of 25.0 literes?

(Ans:31.7 ^{0}C/304.9 K)

F. A 20 L container holds 0.650 mol of He gas at 37^0C at a pressure of 628.3 bar. What will be new pressure inside the container if the volume is reduced to 12 L. The temperature is increased to 177 ^{0}C and 1.25 mol of additional He gas was added to it?

(Ans:4443 bar/4385 atm)

G. Nitrogen gas is filled in a container of volume 2.32 L at 32^0C and 4.7 atm pressure. Calculate the number of moles of the gas.

(Ans:0.436 moles)

H. At 25 ^{0}C and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at the height where temperature is 10 ^{0}C and volume of the gas 640 mL ?

(Ans : 676.6 mm Hg)

I. A neon-dioxygen mixture contains 70.6 g dioxygen and 167.5g neon.If pressure of the mixture of the gases in the cylinder is 25 bar. What is the partial pressure of dioxygen and neon in the mixture?

(Ans:p_{O_2}= 5.25 bar, p_{Ne}=19.75 bar)

J. Calculate the pressure in atm of 1.0 mole of helium in a 2.0 dm^3 container at 20.0^0C.

(Ans:12.02 atm)

K. Calculate the volume of 1 mole of a gas at exactly 20 ^{0}C at a pressure of 101.35 kPa.

(Ans: 24.055 dm^3)

L. Calculate the number of molecules of methane in 0.50 m^3 of the gas at a pressure of 2.0×10^2 kPa and a temperature of exactly 300 K.

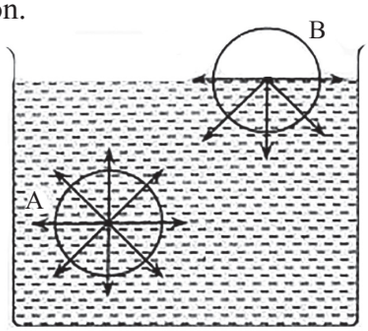
(Ans: 2.4×10^{25})

Activity :

Perform different activities related to concepts mentioned in chapter.

11. Adsorption and Colloids

11.1 Introduction : When a metal spoon is dipped in milk and taken out, you will notice that a film of milk particles cover the spoon surface. If a cold water bottle is taken out from the refrigerater and kept on a table for a while, water vapour is seen to condense on the outer surface of the bottle, forming droplets or a film. Here the milk particles or the water molecules from the air get adsorbed on the surface of the spoon and the bottle. Surfaces of all the objects around us are exposed to the atmosphere. Water molecules as well as other gas molecules such as N_2, O_2, from the air form an invisible multi molecular film on these objects. This is known as the phenomenon of adsorption.



A - Bulk molecule
B - Surface molecule

Fig 11.1 Unbalanced forces

11.2. Adsorption :

11.2.1 Unblanced forces : Consider a surface of liquid or solid. The molecular forces at the surface of a liquid are unbalanced or in unsaturation state. In solids, the ions or molecules at the surface of a crystal do not have their forces satisfied by the close contact with other particles.

Because of the unsaturation solid and liquid surfaces tend to attract gases or dissolved substances with which they come in close contact. Thus the substance accumulates on the surface of solid or liquid.

Can you tell?

What is adsorption ?

11.2.2 Why does adsorption occur?

The adsorption phenomenon is caused by London dispersion forces or van der Waals forces. These are short range and additive. The adsorption force is the sum of all interactions between all the atoms. The pulling interactions cause the surface of a liquid to tighten like an elastic film. A measure of the elastic force at the surface of a liquid is called surface tension. (Refer to Chapter 10).

The surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area. There is a tendency to have minimum surface tension that is, decrease of free energy, which leads to adsorption. Terms involved in adsorption :

Adsorbent : The material or substance present in the bulk, on the surface of which adsorption takes place is called adsorbent.

Adsorbate : The substance getting absorbed on the the adsorbent is called as adsorbate.

11.2.3 Examples of Absorption: You know that when cotton is dipped in water, cotton becomes wet with water which is due to absorption.

Some more examples of adsorption :

i. Adsorption of gases like hydrogen, oxygen, by finely divided metals, namely, platinum, palladium, copper, nickel, etc.

ii. Adsorption of gases like nitrogen, carbondioxide, by activated charcoal.

iii. Removal of colouring matter like an organic dye, for example methylene blue. When charcoal is added to methylene blue solution and shaken, it becomes colourless after some time, as dye molecules accumulate on the surface of charcoal.

Table 11.1 shows comparison between adsorption and absorption.

11.2.4 Desorption: The process of removal of an adsorbed substance from a surface on which it was adsorbed is called desorption.

Table 11.1 : Comparison between Adsorption and Absorption

Adsorption	Absorption
1. Adsorbed matter is concentrated only at the surface and does not penetrate through the surface to the bulk of adsorbent. Adsorption is a surface phenomenon.	Absorbed matter is uniformly distributed inside as well as on the surface of the bulk of substance. Absorption is a bulk phenomenon.
2. Concentration of the adsorbate is high only at the surface of the adsorbent.	Concentration of the absorbate is uniform throughout the bulk of the absorbent.
3. It is dependent on temperature and pressure.	It is independent of temperature and pressure.
4. It is accompanied by evolution of heat known as heat of adsorption.	It is not accompanied by evolution or absorption of heat.
5. It depends on surface area	It is independent of surface area.
6. Example: Adsorption of a gas or liquid like acetic acid by activated charcoal	Example : Absorption of water by cotton. Absorption of ink by blotting paper.

Try this

Dip a chalk in ink. What do you observe ?

11.2.5 Sorption: When a chalk is dipped in ink, ink molecules are adsorbed at the surface of chalk and the surface becomes coloured, while the solvent of the ink goes deeper into the chalk due to absorption. When, both adsorption and absorption occur simultaneously it is known as sorption.

11.3 Types of adsorption: There are mainly two types of adsorption phenomenon depending on nature of forces involved.

11.3.1 Physical Adsorption or physisorption:

When the adsorbent such as gas molecules are accumulated at the surface of a solid on account of weak van der Waals forces, the adsorption is termed as physical adsorption or physisorption.

The van der Waals forces, are similar to forces causing condensation of gas into liquid. Thus, heat is released in physisorption. The heat released during physisorption is of the same order of magnitude as heat of condensation. Due to weak nature of van der Waals forces, physisorption is also weak in nature. The adsorbed gas forms several layers of molecules at high pressures. The extent of adsorption is large at low temperatures. The equilibrium is attained rapidly. The physisorption is readily reversed by lowering of pressure of gas or by raising temperature.

11.3.2 Chemical Adsorption or Chemisorption : Chemisorption was first investigated in 1916 by American Chemist, **Irving Langmuir** (1881-1957). When the gas molecules accumulate on the surface of a solid or adsorbate by means of chemical bonds, be it covalent or ionic, the adsorption is called chemical adsorption (or chemisorption). Chemisorption is specific in nature. Chemisorption involving the gas-solid as the adsorbate and adsorbent, is usually exothermic. It means that heat is released during this process. (Exception : the adsorption of hydrogen on glass is endothermic : heat is absorbed during the process. This is due to dissociation of hydrogen.) The heat evolved in chemisorption per mole of adsorbate is nearly the same order of magnitude as that accompaning chemical bonding. Chemisorption involves a large energy of activation and referred as activated adsorption. Chemisorption increases with increase in temperature in the beginning, as more number of molecules can have activation energy. But after certain temperature chemisoption decreases with increase in temperature, as the chemical bonds break.

Sometimes at low temperature, physisorption occurs which passes into chemisorption as the temperature is raised. Besides, chemisorption is dependent on surface area of the adsorbent (See Table 11.2).

Table 11.2 : Comparison of physisorption and chemisorption

Physisorption	Chemisorption
1. The forces operating are weak van der Waals forces.	1. The forces operating are chemical nature (covalent or ionic bonds).
2. Not specific in nature. All gases adsorb on all solids. For example, all gases adsorb on charcoal.	2. Highly specific and occurs only when chemical bond formation is possible between adsorbent and adsorbate. For example, adsorption of oxygen on tungsten, hydrogen on nickel, etc.
3. The heat of adsorption is low and lies in the range 20 - 40 kJ mol^{-1}	3. Higher heat of adsorption and lies in the range 40 - 200 kJ mol^{-1}
4. Occurs at low temperature and decreases with an increase of temperature.	4. Favoured at high temperature, the extent of chemical adsorption is lowered at very high temperature, due to bond breaking.
5. For example : at low temperature N_2 gas is physically adsorbed on iron.	5. For example N_2 gas chemically adsorbed on iron at high temperature forms a layer of iron nitride, which desorbs at very high temperature.
6. Reversible.	6. Irreversible.
7. Physisorbed layer may be multimolecular layer, of adsorbed particles under high pressure.	7. Chemisorption forms monomolecular layer of adsorbed particles.

11.4 Factors affecting adsorption of gases on solids : All solids adsorb gases to some extent. The extent of adsorption depends upon a number of factors discussed in this section.

1. Nature of adsorbate (gas) : The amount of gas adsorbed by a solid depends on the nature of the gas. Gases having high critical temperature liquify easily and can readily be adsorbed. (Refer to chapter 10). The gases such as SO_2, Cl_2, NH_3 which are easily liquifiable are adsorbed to a large extend compared to N_2, O_2, H_2 etc, which are difficult to liquify.

Table 11.3 : Critical temperature of gases and volume adsorbed

Gas	Critical temperature/K	Volume adsorbed/ cm^3
N_2	126	08
HCl	324	72
NH_3	406	181
Cl_2	417	235
SO_2	430	380

2. Nature of adsorbent: Substances which provide large surface area for a given mass are effective as adsorbents and adsorb appreciable volumes of gases. Silica gel, charcoal are effective adsorbents due to their porous nature.

3. Surface area of adsorbent : Adsorption is a surface phenomenon. Hence, the extent of adsorption increases with increase in surface area of adsorbent. Finely divided substances, rough surfaces, colloidal substances are good adsorbents as they provide larger surface area for a given mass.

4. Temperature : Adsorption is an exothermic process. According to Le-Chatelier's principle (Chapter 12), it is favoured at low temperature. The amount of gas adsorbed is, thus, inversely proportional to temperature.

Figure 11.2 shows plots of volume of N_2 adsorbed per unit mass of adsorbent against the pressure of a gas at different temperatures. As temperature increases from 193 K to 273 K at a constant pressure 'P' the amount of gas adsorbed decrease.

5. Pressure of gas : At any temperature, the extent of gas adsorbed increases with an increase of pressure. The extent of adsorption is directly proportional to pressure of the gas. At high pressures extent of adsorption becomes independent of the pressure. The surface of adsorbent is, then, almost fully covered by adsorbed gaseous molecules.

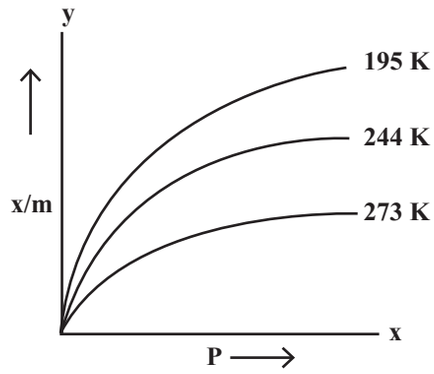


Fig 11.2 Variation of adsorption with temperature and pressure

11.5 Adsorption Isotherm : The relationship between the amount of a substance adsorbed per unit mass of adsorbent and the equilibrium pressure (in case of gas) or concentration (in case of solution) at a given constant temperature is called an adsorption isotherm. Various adsorption isotherms are known.

Freundlich adsorption isotherm : Freundlich proposed an empirical equation for adsorption of a gas on solid.

$$\frac{x}{m} = k P^{1/n} \quad (n>1) \qquad \ldots\ldots\ldots (11.1)$$

Where x = mass of the gas adsorbed

m = mass of the adsorbent at presure P

$\frac{x}{m}$ = mass of gas adsorbed per unit mass of adsorbent

P = equilibrium pressure.

k and n are constants which depend on the nature of adsorbate, adsorbent and temperature.

Graphical Representation of Freundlich equation.

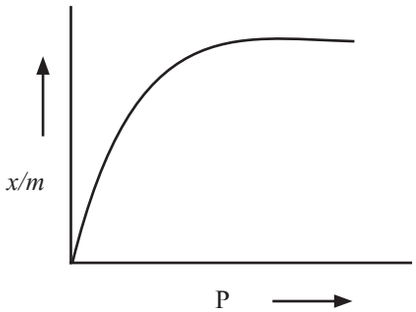


Fig 11.3 Adsorption isotherm

In case of solution, P in the Eq. (11.1) is replaced by the concentration and thus

$$\frac{x}{m} = kC^{1/n} \qquad \ldots\ldots\ldots (11.2)$$

After taking logarithm of the above Eq. 11.2

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C \qquad \ldots\ldots\ldots (11.3)$$

Plotting $\log \frac{x}{m}$ against $\log C$ or $\log P$, a straight line is obtained which is shown in Fig.11.4.

The slope of the straight line gives $\frac{1}{n}$. While intercept on y-axis gives log k. The factor $\frac{1}{n}$ ranges from 0 to 1. Equation (11.3) holds good over limited range of pressures.

When $\frac{1}{n} \rightarrow 0$, $\frac{x}{m} \rightarrow$ constant, the adsorption, then, is independent of pressure.

When $\frac{1}{n} = 1$, $\frac{x}{m} = kP$. i.e. $\frac{x}{m} \alpha P$ the adsorption varies directly with pressure. The experimental isotherms as in Fig. 11.3 tend to saturate at the high pressure.

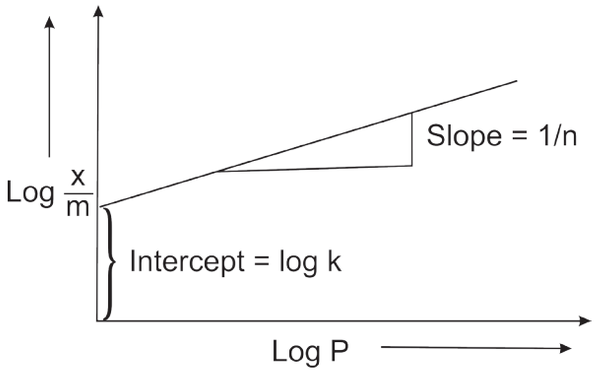


Fig. 11.4 : Freundlich isotherm

11.6 Applications of Adsorption :

The adsorption finds large number of applications as illustrated here.

i. Catalysis: Heterogeneous catalysis : The solid catalysts are used in many industrial manufacturing processes. For example, iron is used as the catalyst in manufacturing of ammonia; platinum in manufacturing of sulphuric acid, H_2SO_4 (by contanct process). In hydrogenation of oils, finely divided nickel is employed as catalyst.

ii. **Gas masks:** It is a device which consists of activated charcoal or mixture of adsorbents. It is used for breathing in coal mines to avoid inhaling of the poisonous gases.

iii. **Control of humidity :** Silica and alumina gels are good adsorbents of moisture.

iv. **Production of high vacuum :** Lowering of temperature at a given pressure, increases the rate of adsorption of gases on charcoal powder. By using this principle, high vacuum can be attained by adsorption. A vessel evacuated by vacuum pump is connected to another vessel containing coconut charcoal cooled by liquid air. The charcoal adsorbs the remaining traces of air or moisture to create a high vacuum.

v. **Adsorption Indicators :** The adsorption is used to detect the end point of precipitation titrations. Dyes such as eosin, fluorescein are used as indicators. For example, A solution of sodium chloride containing a small amount of fluorescein is titrated against silver nitrate solution.

$$NaCl + AgNO_3 \rightarrow \underset{\text{White ppt}}{AgCl} + NaNO_3$$

When chloride ions are over, fluorescein is adsorbed on white silver chloride precipitate and red colour is developed. Thus colour change from pale yellow to reddish pink is observed at the end point.

vi. **Separation of inert gases :** In a mixture of noble gases, different gases adsorb to different extent. Due to selective adsorption principle, gases can be separated on coconut charcoal.

vii. **Froth floatation process :** A low grade sulfide ore is concentrated by separating it from silica and other earthy matter using pine oil as frothing agent. Hydrophobic pine oil preferentially wets (adsorbs on) sulfide ore which is taken up in the froth.

viii. **Chromatographic analysis :** It is based on selective adsorption of ions from solution using powdered adsorbents such as silica or alumina gel. It has several industrial and analytical applications. Other applications include surface area determination, purification of water, etc.

11.7 Catalysis : Catalysts are of importance in chemical industry and in living organisms. A large number of the chemicals manufactured in industries make use of catalysts to obtain specific products, The use of catalyst lowers the reaction temperature, and energy costs significantly.

A **catalyst** thus can be defined as a **substance which when added to a reacting system increases the rate of a reaction without itself undergoing any permanent chemical change**. Catalysis is of two types, namely homogeneous an heterogeneous catalysis.

11.7.1 Homogeneous Catalysis : When the reactants and the catalyst are in the same phase, it is said to be homogenous catalysis.

Examples of homogeneous catalysis:

i. Iodide ion ($I^{\ominus}$) finds use as homogeneous catalyst in decomposition of aqueous hydrogen peroxide (Both $I^{\ominus}$ and H_2O_2 are present in the same aqueous phase)

ii. Oxidation of sulfur dioxide to sulfur trioxide with dioxygen (O_2) in the presence of nitirc oxide as catalyst (lead chamber process).

$$2\,SO_2\,(g) + O_2\,(g) \xrightarrow{NO(g)} 2\,SO_3\,(g)$$

iii. Hydrolysis of sugar is catalysed by $H^{\oplus}$ ion furnished by sulphuric acid.

$$\underset{\text{Sucrose solution}}{C_{12}H_{22}O_{11}\,(aq)} + H_2O\,(l) \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6\,(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6\,(aq)}$$

All reactants and catalyst are in same solution phase.

iv. Enzyme catalysis is also an important type of homogeneous catalysis.

11.7.2 Heterogeneous Catalysis : When the reactant and catalyst are in different phase, it is said to be heterogeneous catalysis.

The heterogeneous catalyst is generally a solid and the reactants may either be gases

or liquids. The solid catalyst is added to the reaction mixture. It does not dissolve in the reacting system. The reaction occurs on surface of solid catalyst.

Examples of heterogeneous catalysis:

i. Dinitrogen (N_2) and dihydrogen (H_2) combine to form ammonia in Haber process in presence of finely divided iron along with K_2O and Al_2O_3.

$$N_2\,(g) + 3\,H_2(g) \xrightarrow[K_2O,\,Al_2O_3]{Fe(s)} 2\,NH_3\,(g)$$

Here Al_2O_3 and K_2O are promoters of the Fe catalyst. Al_2O_3 is added to prevent the fusion of Fe particles. K_2O causes chemisorption of nitrogen atoms. Molybdynum is also used as promoter.

ii. Hydrogenation reaction of vegetable oils to produce solid fat is used in food industry. The reaction is catalysed by finely divided metals like Ni, Pd or Pt. Vegetable oil contains one or more carbon carbon double bonds (C = C) in its structure. On hydrogenation a solid product (which contains only carbon carbon single bonds) is formed. It is called *vanaspati ghee*.

Vegetable oil $(l) + H_2\,(g) \xrightarrow{Ni\,(s)}$ Vegetable ghee(s)

(C = C) (C - C)

iii. Another important application of heterogenous catalysts is in automobile catalytic converters. In automobile exhaust, large number of air pollutants such as carbon monoxide, nitric oxide, etc. are present. The catalytic converter transforms the air pollutants into carbon dioxide, water, nitrogen and oxygen. The catalyst is poisoned by the adsorption of Pb (lead). The automobiles with catalytic converter require unleaded petrol.

11.7.3 Inhibitors : Inhibitors are substances those decrease rate of chemical reaction.

Examples,

i. Chlorofom was once used as anaesthetic. It forms poisonous substance, carbonyl chloride by air oxidation.

$$4\,CHCl_3\,(l) + 3\,O_2\,(g) \rightarrow 4\,COCl_2\,(g) + 2\,H_2O\,(l) + 2\,Cl_2\,(g)$$

When 2% ethanol is added to chloroform, the formation of $COCl_2$ is suppressed. Ethanol acts as an inhibitor and retards the above reaction.

ii. Hydrogen peroxide decomposes as,

$$2\,H_2O_2\,(l) \rightarrow 2\,H_2O\,(l) + O_2\,(g)$$

The reaction is inhibited by addition of dilute acid or glycerol acting as inhibitor.

11.8 Adsorption Theory of Heterogeneous catalysis: The catalytic action occurs on the surface of a catalyst. The mechanism involves five steps.

i. Diffusion of reactants toward the surface of the catalyst.
ii. Adsorption of reactant molecules on the surface of the catalyst.
iii. Occurrence of chemical reaction on the catalyst surface and formation of an intermediate.
iv. Formation of products.
v. Desorption of reaction products from the catalyst surface. Products leave catalyst surface.

The steps involved can be shown as :

Diffusion → Adsorption → intermediate formation

↓

Desorption ← Product formation

Fresh reactant molecules can replace the products to start the cycle again as in step (i). This explains why catalyst remains unchanged in mass and chemical composition at the end of the reaction.

11.8.1 Important features of solid catalysts:

a. Catalytic activity : The activity of a catalyst depends on the strength of chemisorption. If large number of reactant molecules (gas or liquid) are strongly adsorbed on the surface of solid catalyst, the catalyst is said to be active. However, the adsorption of reactant molecules on the surface, that is, the bond formed between adsorbate and adsorbent surface should not be very strong so that they are not immobilized.

It has been found that d-block metals such as Fe, V and Cr tend to be strongly active toward O_2, C_2H_2, C_2H_4, CO, H_2, CO_2, N_2 etc; Mn and Cu are unable to adsorb N_2 and CO_2. The metals Mg and Li adsorb O_2 selectively.

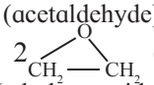
b. Catalytic selectivity : Some solid catalysts are selective in their action. The same gaseous reactants produce different products when different catalysts are used.

For example,

i. The gaseous ethylene and O_2 react to produce different products with different catalysts.

a. $C_2H_4(g) + O_2(g) \xrightarrow{Pd/Al_2O_3} 2\ CH_3CHO(g)$

(ethylene) (acetaldehyde)

b. $2\ C_2H_4(g) + O_2(g) \xrightarrow{Ag/Al_2O_3} 2$  (g)

(ethylene) (ethylene oxide)

ii. The gaseous carbon monoxide and H_2 produce different products by using different catalysts.

a. $CO(g) + 3\ H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

b. $CO(g) + 2\ H_2(g) \xrightarrow{Cu/ZnO\text{-}Cr_2O_3} CH_3OH(g)$

c. Shape selective catalysis by zeolites :

Zeolites are alumino silicates with three-dimensional network of silicates. Some silicon atoms in this network are replaced by aluminium atoms giving Al-O-Si frame work. This results in microporous structure. The reactions in zeolites are dependent on the size and shape of reactant or products and also on pores and cavities of zeolites. Zeolites, therefore, are shape selective catalysts.

In petroleum industry, zeolite catalyst ZSM-5 converts alcohols directly to gasoline (pertol) by dehydration which gives a mixture of hydrocarbons.

11.9 Colloids : A number of substances we use in our day to day life are colloids. For example, milk, butter, jelly, whipped cream, mayonnaise. Colloid chemistry is the chemistry of everyday life. Knowledge of colloid chemistry is essential for understanding about many useful materials like cement, bricks, pottery, porcelain, glass, enamels; oils, lacquers; rubber, celluloid and other plastics, leather, paper, textiles, filaments, crayons, inks, road construction material etc. In many daily processes like cooking, washing, dyeing, painting, ore floatation, water purification, sewage disposal, smoke prevention, photography, pharmacy, use of colloids is important.

Colloids are heterogeneous mixtures. The component of colloid present in the largest proportion is called **dispersion medium** and the other components are called **dispersed phase**. The particles of the dispersed phase are larger than the size of a molecule and smaller than particles which we can see with naked eye.

Observe the formation of solution of salt and water. Salt dissolves completely in water and forms homegeneous system. On the other hand ground coffee or tea leaves with milk form suspension. Between the two extremes of solution and suspension, we observe a large group of systems called colloidal dispersions or simply colloids.

The essential difference between a solution and a colloid is particle size. **Solutions** contain solute particles with diameter in the range 0.1 to 2 nm, the size of typical ion or small molecule. Solutions are **transparent** and may be coloured and do not separate on standing. On the other hand, **colloids** such as milk, fog contain particles of dispersed phase with diameters in the range at 2 to 500 nm. They are **transluent** to light and do not separate on standing.

11.9.1 : Exaples of colloids : Some examples of phenomenon observed in our daily life, which are understood in terms of colloids are as follows :

i. Blue colour of the sky : The sky appears blue to us because minute dust particles along with minute water droplets dispersed in air scatter blue light which reaches our eyes.

ii. Blood : It is a colloidal dispersion of plasma proteins and antibodies in water. (At the same time blood is also a suspension of blood cells and platelets in water.)

iii. Soils : Fertile soils are colloidal in nature where humus acts as a protective colloid. Soil adsorbs moisture and nourishing materials due to its colloidal nature.

Table 11.4 :Types of colloids based on physical state

Dispersed phase	Dispersion medium	Type of colloid	Examples
solid	solid	solid sol	coloured glasses, gem stones, porcelain, paper
solid	liquid	sols and gels	paints, cell fluids, gelatin, muddy water, starch solution.
solid	gas	aerosol	smoke, dust
liquid	solid	gel	cheese, butter, jellies
liquid	liquid	emulsion	milk, hair cream
liquid	gas	aerosol	fog, mist, cloud, hair sprays, insecticide sprays.
gas	solid	solid sol	pumice stone, foam rubber, plaster
gas	liquid	foam	froth, whipped cream, soap lather

Table 11.5 : Distinction between Lyophilic and Lyophobic colloids

Lyophilic colloids	Lyophobic colloids
1. Formed easily by direct mixing.	Formed only by special methods.
2. Reversible.	Irreversible.
3. The particles are not easily visible even under ultramicroscope.	The particles are easily detected under ultramicroscope.
4. These are self stabilized.	These are unstable and hence require traces of stabilizers.
5. Addition of **large amount of electrolytes** causes precipitation/coagulation.	Addition of **small amount of electrolytes** causes precipitation/ coagulation.
6. Viscosity of dispersed phase much higher than that of the dispersion medium.	Viscosity of dispersed phase is nearly the same as the dispersion medium.
7. Surface tension of dispersed phase is lower than dispersion medium.	Surface tension of dispersed phase is nearly the same as the dispersion medium.

iv. Fog, mist and rain : Mist is caused by small droplets of water dispersed in air. Fog is formed whenever there is temperature difference between ground and air. A large portion of air containing dust particles gets cooled below its dew point, the moisture from the air condenses on the surface of these particles which form fine droplets, which are colloid particles and float in air as fog or mist.

11.9.2 Classification of colloids : Colloids are classified in three different ways.

a. Classification of colloids based on physical state : Table 11.4 illustrates the types of colloids in accordance with the physical states of dispersed phase and dispersion medium.

b. Classification of colloids based on interaction or affinity of phases : On the basis of interaction or affinity of phases, a colloidal solution is classified as lyophilic and lyophobic. If water is dispersion medium, the terms hydrophilic and hydrophobic are used.

i. Lyophilic colloids: Lyo means liquid and philic means loving. A colloidal solution in which the particles of dispersed phase have a great affinity for the dispersion medium are lyophilic colloids. If the lyophilic sol is evaporated, the dispersed phase separates. But if it is remixed with the medium, the sol can be formed again. That is why such sols are called reversible sols. They are stable and difficult to coagulate.

ii. Lyophobic colloids: Colloidal solution in which the particles of the dispersed phase have no affinity for the dispersion medium are lyophobic colloids. Phobic means fearing, hence liquid hating. The common examples are Ag, Au, hydroxides like $Al(OH)_3$, $Fe(OH)_3$, metal sulfides. Once precipitated/coagulated they have little tendency or no tendency to revert back to colloidal state.

Table 11.5 shows comparison of lyophilic and lyophobic colloids.

c. Classification of colloids based on molecular size : Colloids are classified into three types in accordance with size of their molecules.

i. Multimolecular Colloids : The individual particles consist of an aggregate of atoms or small molecules with size less than 10^3 pm. For examples : **Gold sol** consists of particles of various sizes having several gold atoms. Colloidal solution in which particles are held together with van der Waals force of attraction is called multimolecular colloid. For Example, S_8 sulfur molecules.

ii. Macromolecular colloids : The molecules of the dispersed phase are sufficiently large in size (macro) to be of colloidal dimensions. Examples are starch, cellulose, proteins, polythene, nylon, plastics.

iii. Associated colloids or micelles : The substances behave as normal electrolytes at low concentration and associated in higher concentration forming a colloidal solution. The associated particles are called Micelles. For example, soap, detergent. Soap molecule

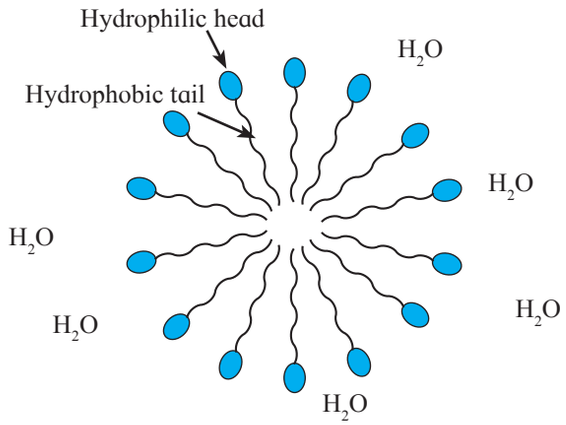


Fig. 11.5 : Soap micelle in water

has a long hydrophobic hydrocarbon chain, called **tail**, attached to hydrophilic ionic group (carboxylate), called **head**. In water the soap molecules arrange themselves to form spherical particles that are called **micelles**. (Fig. 11.5) In each micelle the hydrophobic tails of soap molecules point to the centre and the hydrophilic heads lie on the surface of the sphere. As a result of this, soap dispersion in water is stable.

11.9.3 Preparation of Colloids : A few important methods for the preparation of colloids are as follows :

a. Chemical methods : By double decomposition, oxidation, reduction or hydrolysis. Molecules of water insoluble products of these reaction aggregate together and form sols.

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} 3S\downarrow + 2H_2O$$

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au\downarrow + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3\downarrow + 3HCl$$

b. Electrical disintegration by Bredig's Arc method : This process involves vaporization as well as condenstion. Colloidal sols of metals such as gold, silver, platinum can be prepared by this method.

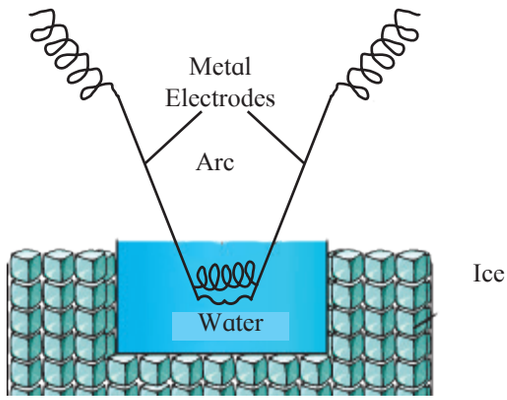


Fig. 11.6 : Bredig's arc method

In this method, electric arc is struck between electrodes of metal immersed in the dispersion medium. The intense heat produced vapourises the metal which then condenses to form particles of colloidal sol.

c. Peptization : During peptization a precipitate is converted into colloidal sol by shaking with dispersion medium in the presence of a small amount of an electrolyte. The electrolyte used, is known as peptizing agent.

During the process, the precipitate adsorbs one of the ions of the electrolyte on its surface, positive or negative charge is developed on the precipitate which finally breaks up into small particles of colloidal size.

11.9.4 Purification of colloidal solution :

Colloidal solution generally contains excessive amount of electrolytes and some other soluble impurities. A small quantity of an electrolyte is necessary for the stability of colloidal solution. A large quantity of electrolyte may result in coagulation. It is also necessary to reduce soluble impurities.

"The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution."

Purification of colloidal solution can be carried out using dialysis by the following method.

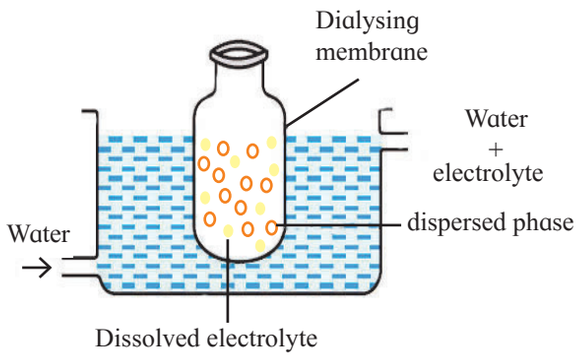


Fig 11.7 : Dialysis

Dialysis : "It is a process of removing a dissolved substance from a colloidal solution by diffusion through a suitable membrane.

The apparatus used is dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing. The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

11.9.5 Properties of colloidal dispersions :

Various properties exhibited by colloidal dispersions are described below.

a. General properties.

i. Colloidal system is heterogeneous and consists of two phases, dispersed phase and dispersion medium.

ii. The dispersed phase particles pass slowly through parchment paper or animal membrane, but readily pass through ordinary filter paper.

iii. The particles usually are not detectable by powerful microscope.

b. Optical property:

Tyndall effect: Tyndall observed that when light passes through true solution the path of light through it cannot be detected.

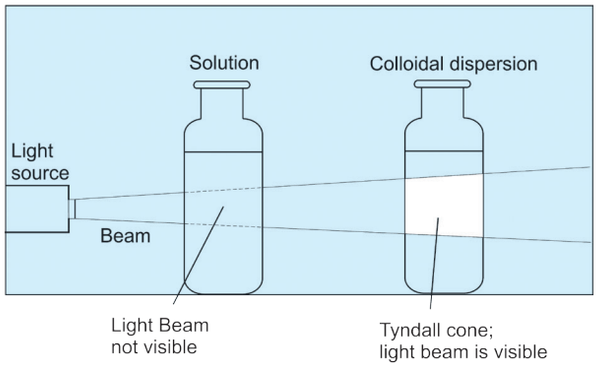


Fig. 11.8 :Tyndall effect

However, if the light passes through a colloidal dispersion, the particles scatter some light in all directions and the path of the light through colloidal dispersion becomes visible to observer standing at right angles to its path.

"The phenomenon of scattering of light by colloidal particles and making path of light visible through the dispersion is referred as Tyndall effect".

"The bright cone of the light is called Tyndall cone". Tyndall effect is observed only when the following conditions are satisfied.

i. The diameter of the dispersed particles is not much smaller than the wavelength of light used.

ii. The refractive indices of dispersed phase and dispersion medium differ largely.

Importance of Tyndall effect:

i. It is useful in determining number of particles in colloidal system and the particle size therein.

ii. It is used to distinguish between colloidal dispersion and true solution.

c. Colour :

i Colour of colloidal solution depends on the wavelength of light scattered by dispersed particles.

The colour of colloidal dispersion also changes with the manner in which the observer receives the light. For example: Mixture of a few drops of milk and large amount of water appears blue when viewed by the scattered light and red when viewed by transmitted light. (Refer to 7th std science book of Balbharati.)

ii. It also depends on size of colloidol particles For example, finest gold sol is red in colour whereas with increase in size it appears purple.

d. Kinetic Property : The colloidal or microscopic particles undergo ceaseless random zig-zag motion in all directions in a fluid. This motion of dispersed phase particles is called Brownian motion. British botanist, Robert Brown, observed such motion of pollen grains under a microscope. The random motion was explained by Albert Einstein in 1905.

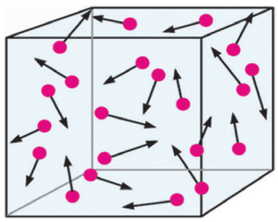


Fig. 11.9 : Brownian motion

Cause of Brownian motion :

i. Constant collision of particles of dispersed phase with the fast moving molecules of dispersion medium (fluid).

ii. Due to this, the dispersed phase particles acquire kinetic energy from the molecules of the dispersion medium. This kinetic energy brings forth Brownian motion.

e. Electrical Properties :

i. Charge on colloidal particles: Colloidal particles carry an electric charge. The nature of this charge is the same on all particles for a given colloidal solution which can be either positive or negative. Some common sols with the nature of charge on the particles are listed in Table 11.6.

Table 11.6 : Charge on dispersed particles

Positively charged sols	Negatively charged sols
1. Hydrated metallic oxides $Al_2O_3 . xH_2O$, $CrO_3 . xH_2O$, $Fe_2O_3 . xH_2O$.	Metals, Cu, Ag, Au Sols metallic sulphides As_2S_3, Sb_2S_3, Cds
2. Basic dye stuff, methylene blue sols	Acid dye stuff, eosin, congo red sol
3. Haemoglobin (blood)	Sols of starch, gum
4. Oxides : TiO_2 sol	Gelatin, clay, gum sols

ii. Electrophoresis : Electrophoresis set up is shown in Fig. 11.10.

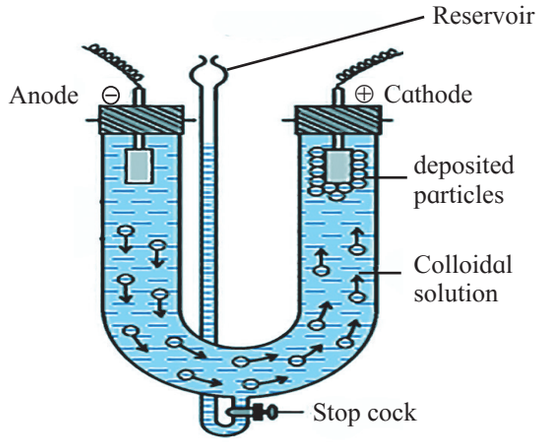


Fig. 11.10 : Electrophoresis

Figure shows U tube set up in which two platinum electrodes are dipped in a collodial solution. When electric potential is applied across two electrodes, collodial particles move towards one or other electrode.

"The movement of colloidal particles under an applied electric potential is called electrophoresis."

Positively charged particles move towards cathode while negatively charged particles migrate to anode and get deposited on the respective electrode.

iii. Electroosmosis : Movement of dispersed particles can be prevented by suitable means, such as use of membrane. Then it is observed that the dispersion medium begins to move in an electric field. This is termed as electroosmosis.

Applications of electrophoresis:

i. On the basis of direction of movement of the colloidal particles under the influence of electric field, it is possible to know the sign of charge on the particles.

ii. It is also used to measure the rate of migration of sol particles.

iii. Mixture of colloidal paticles can be separated by electrophoresis since different colloidal particles in mixture migrate with different rates.

f. Coagulation: 'The precipitation of colloids by removal of charge associated with colloidal particles is called coagulation.'

The charge on the colloidal particles is due to the preferential adsorption of ions on their surface. For precipitation of lyophobic colloids removal of charge is required. A situation with lyophilic colloids is a little different. The lyophilic particles first attract the molecules of dispersion medium and form a layer of medium surrounding the particles, which may adsorb the ions. Hence for the precipitation of lyophilic colloids, removal of charge on layer of medium is necessary.

11.9.6 Methods to effect coagulation : A coagulation of the lyophobic sols can be carried out in the following ways.

i. By electrophoresis : The colloidal particles move towards oppositely charged electrodes, get discharged and precipitate.

ii. By mixing two oppositely charged sols : Oppositely charged sols when mixed in almost equal proportions neutralize their charges and get precipitated.

Example - Mixing of hydrated ferric oxide (positive sol) and arsenious sulfide (negative sol) brings them in the precipitated forms. This type of coagulation is called mutual coagulation.

iii. By boiling : When a sol is boiled, the adsorbed layer is disturbed as a result of increased collisions with molecules in dispersion medium. This reduces charge on the particles and subsequently settling down as a precipitate.

iv. By persistent dialysis: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely. The colloids then become unstable and finally precipitate.

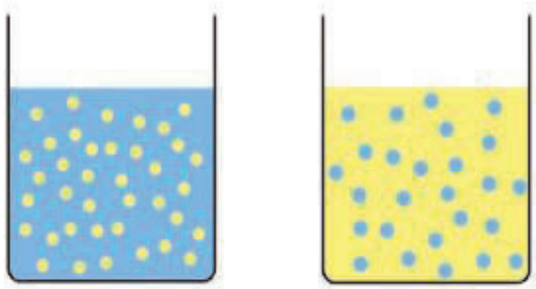
v. By addition of electrolytes : When excess of an electroylte is added, the colloidal particles are precipitated.

Hardy-Schulze rule : Generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy - Schulze rule. In the coagulation of negative sol, the flocculating power follows the order: $Al^{\oplus 3} > Ba^{\oplus 2} > Na^{\oplus}$

Similarly, coagulation of positive sol, reveal : $[Fe(CN)_6]^{4\ominus} > PO_4^{3\ominus} > SO_4^{2\ominus} > Cl^{\ominus}$

11.9.7 Emulsions : A colloidal system in which one liquid is dispersed in another immiscible liquid is called an emulsion. There are liquid-liquid colloidal system in which both liquids are completely or partially immiscible.

Types of emulsions :



Oil in water **Water in oil**

Fig. 11.11 : Emulsions

There are two types of emulsions (Fig. 11.15).

i. Emulsion of oil in water (o/w type) : An emulsion in which dispersed phase is oil and dispersion medium is water is called emulsion of oil in water. For example : milk, vanishing cream, paint etc. Milk consists of particles of fat dispersed in water.

ii. Emulsion of water in oil (w/o type): An emulsion in which dispersed phase is water and dispersion medium is oil is called emulsion of water in oil. For example, codliver oil consists of particles of water dispersed in oil. Some other examples of this type include butter, cream, etc.

Table 11.7 describes difference between the two types of emulsion.

Table 11.7 : Distinction between oil in water and water in oil emulsions

Oil in water	Water in oil
1. Oil is the dispersed phase and water is the dispersion medium.	Water is dispersed phase and oil is the dispersion medium.
2. If water is added, it will be miscible with the emulsion.	If oil is added, it will be miscible with the emulsion.
3. An addition of small amount of an electrolyte makes the emulsion conducting.	Addition of small amount of an electrolyte has no effect on conducting power.
4. Water is continuous phase.	Oil is continuous phase.
5. Basic metal sulfates, water soluble alkali metal soaps are used as emulsifiers.	Water insoluble soaps such as those of Zn, Al, Fe, alkaline earth metals are used as emulsifiers.

Properties of Emulsion :

1. Emulsion can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed forms a separate layer.
2. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes.
3. Emulsions show Brownian movement and Tyndall effect.
4. The two liquids in emulsions can be separated by heating, freezing or centrifuging etc.

11.9.8 Applications of colloids : Colloids find appplications in industry and in daily life. Following are some examples.

i. Electrical precipitation of smoke : Smoke is colloidal solution of solid particles of carbon, arsenic compound, dust etc. in air. When smoke is allowed to pass through chamber containing plates having charged smoke particles they lose their charge and get precipitated.

The particles settle down on the floor of the chamber. The precipitator is called Cottrell precipitator.

ii. Purification of drinking water: Water obtained from natural sources contains colloidal impurities. By addition of alum to such water, colloidal impurities get coagulated and settled down. This makes water potable.

iii. Medicines: Usually medicines are colloidal in nature. Colloidal medicines are more effective owing to large surface area to volume ratio of a colloidal particle, and easy assimilation.

Argyrol is a silver sol used as an eye lotion. Milk of magnesia, an emulsion is used in stomach disorders.

iv. Rubber Industry: - Rubber is obtained by coagulation of latex.

v. Cleansing action of soaps and detergents

vi. Photographic plates, films, and industrial products like paints, inks, synthetic plastics, rubber, graphite lubricants, cement etc. are colloids.

Internet my friend

1. Brownian motion
   https://myoutube.com>watch
2. Collect information about Surface Chemstry.
3. Collect information about Adsorption.
4. Collect information about Brownian Motion

Activity :

Calculate surface area to volume ratio of spherical particle. See how the ratio increases with the raduction of radius of the particle. Plot the ratio against the radius.

Exercises

1. Choose the correct option.

A. The size of colloidal particles lies between-
   a. 10^{-10} m and 10^{-9} m
   b. 10^{-9} m and 10^{-6} m
   c. 10^{-6} m and 10^{-4} m
   d. 10^{-5} m and 10^{-2}m

B. Gum in water is an example of
   a. true solution b. suspension
   c. lyophilic sol d. lyophobic sol

C. In Haber process of production of ammonia K_2O is used as
   a. catalyst b. inhibitor
   c. promotor d. adsorbate

D. Fruit Jam is an example of-
   a. sol b. gel
   c. emulsion d. true solution

2. Answer in one sentence :

A. Name type of adsorption in which vander Waals focres are present.

B. Name type of adsorption in which compound is formed.

C. Write an equation for Freundlich adsorption isotherm.

3. Answer the following questions:

A. Define the terms:
   a. Inhibition
   b. Electrophoresis
   c. Catalysis.

B. Define adsorption. Why students can read black board written by chalks?

C. Write characteristics of adsorption.

D. Distinguish between Lyophobic and Lyophilic sols.

E. Identify dispersed phase and dispersion medium in the following colloidal dispersions.
   a. milk b. blood
   c. printing ink d. fog

F. Write notes on :
   a. Tyndall effect
   b. Brownian motion
   c. Types of emulsion
   d. Hardy-Schulze rule

G. Explain Electrophoresis in brief with the help of diagram. What are its applications ?

H. Explain why finely divided substance is more effective as adsorbent?

I. What is the adsorption Isotherm?

J. Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless. Explain.

K. What happens when a beam of light is passed through a colloidal sol?

L. Mention factors affecting adsorption of gas on solids.

M. Give four uses of adsorption.

N. Explain Bredig's arc method.

O. Explain the term emulsions and types of emulsions.

4. Explain the following :

A. A finely divided substance is more effective as adsorbent.

B. Freundlich adsorption isotherm, with the help of a graph.

5. Distinguish between the following :

A. Adsorption and absorption. Give one example.

B. Physisorption and chemisorption. Give one example.

6. Adsorption is surface phenomenon. Explain.

7. Explain how the adsorption of gas on solid varies with
   a. nature of adsorbate and adsorbent
   b. surface area of adsorbent

8. Explain two applications of adsorption.

9. Explain micelle formation in soap solution.

10. Draw labelled diagrams of the following :
   a. Tyndall effect
   b. Dialysis
   c. Bredig's arc method
   d. Soap micelle

Activity :

Collect the information about methods to study surface chemistry.

12. Chemical Equilibrium

Can you recall?

What are the types of the following changes? Natural waterfall, spreading of smoke from burning inscence stick, diffusion of fragrance of flowers. Can the above changes take place in the opposite direction ?

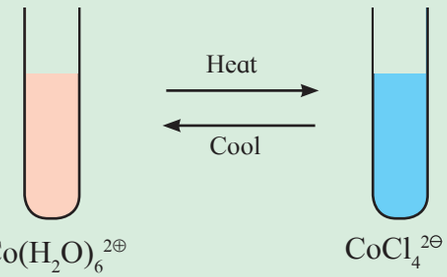
12.1 Introduction : You have learnt earlier that changes can be physical or chemical and reversible or irreversible. All the changes listed above are **irreversible physical changes**. You have also learnt earlier that chemical changes can be represented by chemical reactions when the exact chemical composition of reactants and products is known. In this chapter we are going to look at **reversible chemical reactions**.

12.1.1 Reversible reaction

In the above activity, the change in colour of the solution is caused by the chemical reaction which reverses its direction with change of temperature.

Try this

Dissolve 4 g cobalt chloride in 40 ml water. It forms a redish pink solution. Add 60 ml concentrated HC1 to this. It will turn violet. Take 5 ml of this solution in a test tube and place it in a beaker containing ice water mixture. The colour of solution will become pink. Place the same test tube in a beaker containing water at 90^0 C. The colour of the solution turns blue.



Test tube in cold water Test tube in hot water

$$Co(H_2O)_6^{2\oplus}(aq) + 4Cl^{\ominus}(aq) \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} CoCl_4^{2\ominus}(aq) + 6H_2O(l)$$

(Pink) (Blue)

Can you tell?

What does violet colour of the solution in above indicate ?

The reaction in the above activity is an example of a **reversible reaction**. There are many chemical reactions which appear to proceed in a single direction. For example:

$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$

$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$

These are called **irreversible reactions**. They proceed only in single direction until one of the reactants is exhausted. Their direction is indicated by an arrow (⟶) pointing towards the products in the chemical equation. On the contrary, reversible reactions proceed in both directions. The direction from reactants to products is the **forward reaction,** whereas the opposite reaction from products to reactants is called the **reverse or backward reaction**. A reversible reaction is denoted by drawing two arrows, such that one arrow points in the forward direction and other in the reverse direction (⇌ or ⇄). These two arrows are also referred to as double arrow.

For example :

$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^{\ominus}(aq) + H_3O^{\oplus}$

Consider an example of decomposition of calcium carbonate. Calcium carbonate when heated strongly, decomposes to form calcium oxide and carbon dioxide. Let us consider what happens if this reaction is carried out in a closed container/system or open container/system.

Remember

In a closed system, there is no exchange of matter with the surroundings but exchange of heat can occur. In an open system, exchange of both matter and heat occurs with the surroundings. An isolated system does not exchange heat nor matter with surroundings.

If we perform the above reaction at high temperature in a closed system, we find that after certain time, we have some calcium carbonate present along with calcium oxide and carbon dioxide. If we continue the experiment over a longer period of time at the same temperature, we find the concentrations of calcium carbonate, calcium oxide and carbon dioxide are unchanged. The reaction thus appears to have stopped and we say the system has attained the equilibrium. Actually, the reaction does not stop but proceeds in both the directions with equal rates. In other words calcium carbonate decomposes to give calcium oxide and carbon dioxide at a particular rate. Exactly at the same rate the calcium oxide and carbon dioxide recombine and form calcium carbonate.

Such reactions which do not go to completion and occur in both the directions simultaneously are **reversible reactions**. A reversible reaction may be represented in general terms as :

$$\underset{\text{reactants}}{A + B} \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} \underset{\text{products}}{C + D}$$

The double arrow indicates that the reaction is reversible.

Consider the reaction of decomposition of calcium carbonate occuring in an open system or container. It is seen that during decomposition of calcium carbonate in an open vessel, carbon dioxide can escape away. Hence calcium carbonate cannot be obtained back.

Such a reaction is **irreversible reaction** which occurs only in one direction, namely, from reactants to products.

Reactions are chemically represented as follows

General representation :

$CaCO_3(s) \xrightarrow{heat} CaO(s) + CO_2(g)$

represents the irreversible reaction in an open container. On the other hand the reversible reaction in closed container is represented as

$$CaCO_3(s) \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} CaO(s) + CO_2(g)$$

Do you know ?

Calcium oxide is also known as quicklime or lime. When heated strongly it glows bright white. In old times this was used in theatre lighting, which gave rise to the phrase *'in the limelight'*.

Internet my friend

Find out the information :

1. Equilibrium existing in the formation oxyhaemoglobin in human body.
2. Refrigeration system in equilibrium.

12.2 Equilibrium in physical processes

(a) Liquid - Vapour equilibrium

Let us now look at a reversible physical process of evaporation of liquid water into water vapour in a closed vessel (see Fig. 12.1).

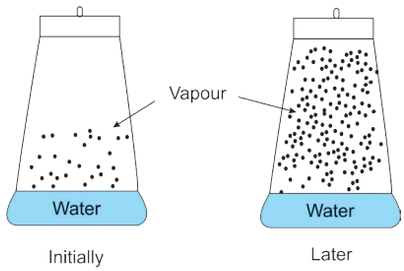


Fig. 12.1 : Water in a closed flask

Initially there is practically no vapour in the vessel. When a liquid evaporates in a closed container, the liquid molecules escape from the liquid surface into vapour phase building up vapour pressure. They also condense back into liquid state because the container is closed. In the beginning the rate of evaporation is high and the rate of condensation is low. But with time, as more and more vapour is formed, the rate of evaporation goes down and the rate

of condensation increases. Eventually the two rates become equal. This gives rise to a constant vapour pressure. This state is known as an '**equilibrium state**'. In this state, the number of molecules leaving the liquid surface equals the number of molecules returning to the liquid from the vapour state. Across the interface, there is a lot of activity between the liquid and the vapour. This state, when the rate of evaporation is equal to the rate of condensation is called equilibrium state. It may be represented as :

$$H_2O(l) \rightleftharpoons H_2O \text{ (vapour)}$$

At equilibrium, the pressure exerted by the gaseous water molecules at a given temperature remains constant, known as the equilibrium vapour pressure of water (or **saturated vapour pressure** of water or **aqueous tension**). The saturated vapour pressure increases with increase of temperature. In the case of water, the saturated vapour pressure is 1.013 bar (1atm) at 100 ^{0}C. Therefore, water boils at 100 ^{0}C when exposed to 1 atm pressure. For any pure liquid at 1 atm pressure the temperature at which its saturated vapour pressure equals to atmospheric pressure is called the normal boiling point of that liquid. The boiling point of water is 100° C at 1.013 bar pressure, whereas the boiling point of ethyl alcohol is 78 ^{0}C.

(b) Solid - liquid equilibrium

Consider a mixture of ice and water in a perfectly insulated thermos flask at 273 K. This is an isolated system. It is an example of solid-liquid equilibrium. Ice and water are at constant temperature. They remain in what is called solid-liquid equilibrium.

(c) Solid - vapour equilibrium :

Try this

1. Place some iodine crystals in a closed vessel. Observe the change in colour intensity in it.

After some time the vessel gets filled up with violet coloured vapour.

The intensity of violet colour becomes stable after certain time.

What do you see in the flask (see Fig. 12.2)?

Fig. 12.2 Solid iodine in equilibrium with its vapour

We see both, that is, solid iodine and iodine vapour in the closed vessel. It means solid iodine sublimes to give iodine vapour and the iodine vapour condenses to form solid iodine. The stable intensity of the colour indicates a state of equilibrium between solid and vapour iodine. We can write the same as follows:

$$I_2 (s) \underset{\text{condensation}}{\overset{\text{sublimation}}{\rightleftharpoons}} I_2(g)$$

Other examples showing this kind of equilibrium are :

1. Camphor (s) $\rightleftharpoons$ Camphor (g)
2. Ammonium chloride (s) $\rightleftharpoons$ Ammonium chloride (g).

Try this

i. Dissolve a given amount of sugar in minimum amount of water at room temperature

ii. Increase the temperature and dissolve more amount of sugar in the same amout of water to make a thick sugar syrup solution.

iii. Cool the syrup to the room temperature.

Note the observation : Sugar crystals separate out.

In a saturated solution there exists dynamic equilibrium between the solute molecules in the solid state and in dissolved state.

$$\text{Sugar (aq)} \rightleftharpoons \text{Sugar (s)}$$

The rate of dissolution of sugar

= The rate of crystallization of sugar

Remember

A saturated solution is the solution when additional solute can not be dissolved in it at the given temperature. The concentration of solute in a saturated solution depends on temperature.

12.3 Equilibrium in chemical process :

If a reaction takes place in a closed system so that the products and reactants cannot escape, we often find that reaction does not give a 100 % yield of products. Instead some reactants remain after the concentrations stop changing. **When there is no further change in concentration of reactant and product, we say that the reaction has attained equilibrium, with the rates of forward and reverse reactions being equal.** Chemical equilibrium at a given temperature is characterized by constancy of measurable properties such as pressure, concentration, density etc. Chemical equilibrium can be approached from either side.

Observe and Discuss

I. Colourless N_2O_4 taken in a closed flask is converted to NO_2 (a reddish brown gas) (See Fig. 12.3)

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

colourless — reddish brown

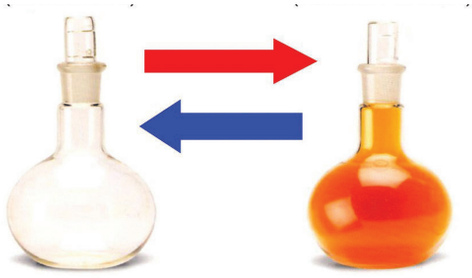


Figure 12.3 : N_2O_4 conversion to NO_2

The colour becomes light brown indicating the presence of NO_2 in the mixture. The formation of NO_2 from N_2O_4 is reversible. In such reaction the reactants react to form the products and the products react to give back reactants.

As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts combining back to form NO_2. At equilibrium, the concentrations of N_2O_4 and NO_2 remain unchanged and do not vary with time, because the rate of formation of N_2O_4 is equal to the rate of formation of NO_2 as shown in Fig. 12.4. b.

II. Consider the following dissociation reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(Colourless gas) — (Violet coloured gas)

The reaction is carried out in a closed vessel starting with hydrogen iodide. The following observations are noted :

1. At first, there is an increase in the itensity of violet colour.
2. After certain time the increase in the intensity of violet colour stops.
3. When contents in the closed vessel are analysed at this stage, it is observed that reaction mixture contains hydrogen iodide, hydrogen and iodine with their concentrations remaining constant over time.

The rate of decomposition of HI becomes equal to the rate of combination of H_2 and I_2. At equilibrium, no net change is observed and both reactions continue to occur.

Let us now see what happens if we start with hydrogen and iodine vapour in a closed container at a certain temperature.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

1. At first, the violet colour if I_2 is deep.
2. The intensity of violet colour starts decreasing.
3. After certain time the decrease in the intensity of colour stops.
4. Analysis of the reaction mixture at this stage shows that it contains HI, H_2 and I_2 with their concentrains remaining constant over time. In other words, the same equilibrium can be attained by starting from any side.

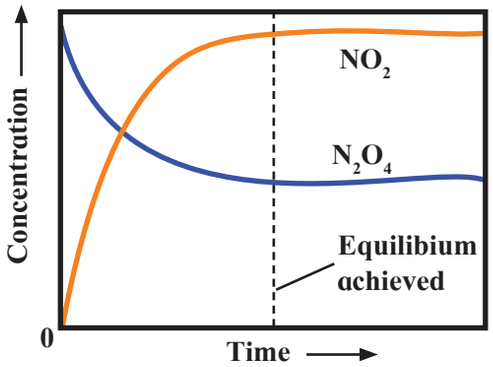


Fig. 12.4 (a) : Graph of forward and reverse reaction rates versus time for conversion of N_2O_4 to NO_2

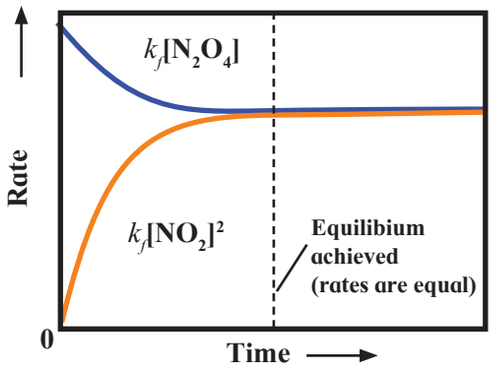


Fig. 12.4 (b) : Changes in reaction rates during a reversible reaction attaining a chemical equilibrium. (Forward rate represented by upper curve in blue and reverse reaction rate lower curve in yellow)

Remember

For any reversible reaction in a closed system the rate of forward reaction is high in the beginning, while the rate of reverse reaction is very slow. As the forward reaction proceeds and products accumulate, rate of forward reaction slows down while rate of reverse reaction increases. Finally the rates become equal and equilibrium is established.

12.4 Law of mass action and equilibrium constant : The chemical equilibrium is mathematically described in terms of what is called the **equilibrium constant (K_C)**. We noted earlier that an equilibrium state is attained when the rate of the forward and reverse reactions become equal (refer Fig. 12.4).

12.4.1 Rate of chemical reaction : As any reaction proceeds the concentration of the reactants decreases and the concentration of the products increases. The rate of reaction thus can be determined by measuring the extent to which the concentration of a reactant decreases in the given time interval, or extent to which the concentration of a product increases in the given time interval. Mathematically, the rate of reaction is expressed as:

$$\text{Rate} = -\frac{\text{d[Reactant]}}{\text{dT}} = \frac{\text{d[Product]}}{\text{dT}}$$

Where d[reactant] and d[product] are the small change in concentration during the small time interval dT.

12.4.2 Law of mass action : The law of mass action states that **the rate of a chemical reaction at each instant is proportional to the product of concentration terms of all the reactants**. In case the balanced chemical equation shows more molecules of reactants, the concentration is raised to a power equal to the number of molecules of that reactant. A rate equation can be written for a reaction by applying the law of mass action as follows :

Consider a reaction $A+B \longrightarrow C$

Here A and B are the reactants and C is the product. The concentrations of chemical species are expressed in mol L^{-1} and denoted by putting the formula in square brackets. By applying the law of mass action to this reaction we write a proportionality expression as :

$\text{Rate} \propto [A][B]$

This proportionality expression is transformed into an equation by introducing a proportionality constant, k, as follows:

$\text{Rate} = k[A][B]$ ....(12.1)

The Eq. (12.1) is called the **rate equation** and the proportionality constant, **k**, is called the **rate constant** of the reaction.

Problem 12.1 : Write the rate equation for the following reaction:

i. $C+O_2 \longrightarrow CO_2$

ii. $2KClO_3 \longrightarrow 2KCl + 3O_2$

Solution : the rate equation is written by applying the law of mass action.

i. The reactants are C and O_2

Rate α $[C]\,[O_2]$

$\therefore$ Rate = k $[C]\,[O_2]$

ii. The reactant is $KClO_3$ and its 2 molecules appear in the balanced equation.

$\therefore$ Rate α $[KClO_3]^2$

$\therefore$ Rate = k $[KClO_3]^2$

12.4.3 Equilibrium constant : Consider a hypothetical reversible reaction $A+B \rightleftharpoons C+D$. As we have noted earlier, two reactions, namely forward and reverse reactions occur simultaneously in a reversible chemical reaction. We, therefore, write rate equations for the forward and reverse reactions:

$\text{Rate}_{\text{forward}} \alpha [A][B]$

$\therefore \text{Rate}_{\text{forward}} = k_f [A]\,[B]$ ..... (12.2)

$\text{Rate}_{\text{reverse}} \alpha [C]\,[D]$

$\therefore \text{Rate}_{\text{reverse}} = k_r [C]\,[D]$ ..... (12.3)

At equilibrium, the rates of forward and reverse reactions are equal. Thus,

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

$\therefore k_f[A]\,[B] = k_r [C]\,[D]$

$$\therefore \frac{k_f}{k_r} = K_C = \frac{[C][D]}{[A][B]} \quad \text{..... (12.4)}$$

Remember

At equilibrium the ratio of product multiplicative term denoting the ratio of concentraton of products to that of the reactants is unchanged and equals K_C. The value of K_C depends upon the temperature. It is interesting to note that though the concentration ratio remains unchanged, both the forward as well as reverse reactions do proceed at equilibrium, but at the same rate. Therefore the chemical equilibrium is a **dynamic equilibrium**.

K_C is called the equilibrium constant.

The equilibrium constant depends on the form of the balanced chemical equation. Consider reversible reaction :

$aA + bB \rightleftharpoons cC + dD$

$$\text{The equilibrium constant } K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{..... (12.5)}$$

If the equilibrium is written as

$cC + dD \rightleftharpoons aA + bB,$

$$K'_C = \frac{[A]^a[B]^b}{[C]^c[D]^d} = \frac{1}{K_C}$$

Thus equilibrium constant of the reverse chemical reaction is K'_C, is the reciprocal of the equilibrium constant K_C of the forward reaction.

Let us consider the equilibrium that occurs in the Haber process for synthesis of ammonia:

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

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} \begin{matrix} \leftarrow \text{coefficient of } NH_3 \\ \leftarrow \text{coefficient of } H_2 \end{matrix}$$

and for the equilibrium reaction written as

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

$$K'_C = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

12.4.3 Equilibrium constant with respect to partial pressure (K_P) : For reactions involving gases, it is convenient to express the equilibrium constant in terms of partial pressure.

$\therefore$ For the reaction,

$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g),$

the equilibrium constant can be expressed using partial pressures (Kp) as given by

$$K_P = \frac{(P_C)^c(P_D)^d}{(P_A)^c(P_B)^d} \quad \text{..... (12.6)}$$

where P_A, P_B, P_C and P_D are equilibrium partial pressures of A, B, C and D, respectively.

Can you recall?

Ideal gas equation with significance of each term involved in it (refer to Chapter 10, section 10.5.5).
PV = nRT, where P is pressure in pascal
n is number of moles of gas
V is volume in dm^3 or L
R is molar gas constant in Pa m^3 K^{-1} mol^{-1}
T is absolute temperature

12.4.4 Relationship between partial pressure and concentration :

For a mixture of ideal gases, the partial pressure of each component is directly proportional to its concentration at constant temperature.

For component A,

$P_A V = n_A RT$

$\frac{n_A}{V}$ is molar concentration of A in mol dm^{-3}

$P_A = \frac{n_A}{V} \times RT$, where $\frac{n_A}{V} = [A]$

$\therefore P_A = [A]RT$

Similarly for components B, C and D the partial pressures are

$P_B = [B]RT$

$P_C = [C]RT$

$P_D = [D]RT$

12.4.5 Relationship between K_P and K_C

Consider a general reversible reaction:

$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

Now substituting expressions for P_A, P_B, P_C, P_D in Eq. (12.6)

$$K_P = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$K_P = \frac{[C]^C [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

$$\therefore K_P = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)}$$

$$\therefore K_P = \frac{[C]^C [D]^d}{[A]^a [B]^b} \times (RT)^{\Delta n}$$

But $K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ from equation (12.5)

$\therefore \boldsymbol{K_P = K_C (RT)^{\Delta n}}$, ... (12.7)

where Δn = (number of moles of gaseous products) - (number of moles of gaseous reactants) in balanced chemical equation.

R = 8.314 L Pa m^3 $K^{-1}mol^{-1}$

While calculating the value of *Kp*, **pressure should be expressed in bar,** because standard pressure is 1 bar.

[1 pascal (Pa) = 1 Nm^{-2} and 1 bar = 10^5 Pa]

Problem 12.2 :

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

Write expression for K_P in terms of *Kc*.

Solution : $K_P = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

$$\therefore K_P = \frac{[NH_3(g)]^2 [RT]^2}{[N_2(g)]RT.[H_2(g)]^3 [RT]^3}$$

$$\therefore K_P = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \times \frac{[RT]^2}{[RT][RT]^3}$$

$\therefore K_P = K_C \times RT^{(2-4)}$

$\therefore K_P = K_C \times RT^{-2}$

Problem 12.3 : Write an expression for K_P and relate it to K_c for the following reversible reaction.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$,

Solution : $K_P = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$

$$\therefore K_P = \frac{[HI(g)]^2 [RT]^2}{[H_2(g)]RT.[I_2(g)]RT}$$

$$\therefore K_P = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \times \frac{[RT]^2}{[RT][RT]}$$

$\therefore K_P = K_C \times RT^{2-(1+1)}$

$\therefore K_P = K_C$

12.5 Homogeneous and Heterogeneous equilibria

12.5.1 Homogeneous reactions and Heterogeneous reactions : In a homogeneous reaction all the reactants are in the same phase. For example is a homogeneous gas phase reaction.

$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$

Reversible reaction involving reactants and products those are in different phases is called heterogeneous reaction.

$NH_3\ (g) + Cl_2\ (g) \rightleftharpoons NH_4Cl\ (s)$

Equilibria involving homogeneous or heterogeneous reactions are called homogeneous and heterogeneous equilibria respectively.

12.5.2 Equilibrium constant for heterogeneous equilibria : As stated earlier, equilibrium having more than one phase is called heterogeneous equilibrium. For example, if ethanol is placed in a conical flask, liquid - vapour equilibrium is established.

$C_2H_5OH(l) \rightleftharpoons C_2H_5OH(g)$

For a given temperature

$$K_C = \frac{[C_2H_5OH(g)]}{[C_2H_5OH(l)]}$$

At any given temperature density of liquid is constant irrespective of the amount of liquid, and, therefore, the term in the denominator is constant. $[C_2H_5OH(l)]$ = constant.

Therefore, the modified equilibrium constant for evaporation of ethanol will be

$K^1_C = K_C$ x constant = $[C_2H_5OH_{(g)}]$

For the equilibrium of sublimation of iodine $I_2(s) \rightleftharpoons I_2(g)$ the modified equilibrium constant $K^1_C = [I_2(g)]$.

Concentrations of pure solids do not change and thus expressions for equilibria including solids are simplified.

Remember

While writing an equilibrium constant expression for heterogeneous reactions use only the concentrations of gases (g) and dissolved substances (aq).

12.5.3 Units of equilibrium constant

The unit of equilibrium constant depends upon the expression of K_C which is different for different equilibria. Therefore, the unit of K_C is also different.

To calculate units of equilibrium constant

Equilibrium Reaction (I)	Equilibrium Reaction (II)
$H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$	$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3(g)$
$K_C = \frac{[HI(g)]^2}{[H_2(g)]\,[I_2(g)]}$ ..... (I)	$K_C = \frac{[NH_3(g)]^2}{[N_2(g)]\,[H_2(g)]^3}$ ..... (II)
Unit of $K_C = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]}$	Unit of $K_C = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]\,[\text{mol dm}^{-3}]^3}$
$= \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]^2}$	$= \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}]^4}$
As all the units cancel out For (I), K_C has no units	$= [\text{mol dm}^{-3}]^{-2}$ $= \text{mol}^{-2}\,\text{dm}^6$

Hint : To calculate units of K_C find out the difference between the number of moles in the numerator and the number of moles in the denominator in the expression for equilibrium constant.

The unit of K_c is $(\text{mol dm}^{-3})^{\Delta n}$.

With reference to expression (II) above,

difference between number of moles =

$\Delta n = 2 - (1+3)$

$\therefore\ \Delta n = 2 - 4$

$\therefore\ \Delta n = -2$

$\therefore$ unit of $K_C = (\text{mol dm}^{-3})^{\Delta n}$

$\therefore$ unit of $K_C = (\text{mol dm}^{-3})^{-2}$

$\therefore$ unit of $K_C = \text{mol}^{-2}\text{dm}^{6}$

Similarly with reference to expression (I) \ unit of $K_C = (\text{mol dm}^{-3})^{\Delta n} = (\text{mol dm}^{-3})^{0}$

$\therefore$ K_C has no unit.

Problem 12.4 : Write the equilibrium constant expression for the decomposition of baking soda. Deduce the unit of K_C from the above expression.

Solution :

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_C = \frac{[Na_2CO_3(s)][CO_2(g)][H_2O(g)]}{[NaHCO_3(s)]^2}$$

$\therefore K_C = [CO_2(g)][H_2O(g)]$

$\therefore$ Unit of $K_C = (\text{mol dm}^{-3})^2 = \text{mol}^2\ \text{dm}^{-6}$

12.6 Characteristics of equilibrium constant

1. The value of equilibrium constant is independent of initial concentrations of either the reactants or products.
2. Equilibrium constant is temperature dependent. Hence K_C, K_P change with change in temperature.
3. Equilibrium constant has a characteristic value for a particular reversible reaction represented by a balanced equation at the given temperature.
4. Higher value of K_C or K_P means more product is formed and the equilibrium point is more towards right hand side and vice versa.

12.7 Application of equilibrium constant

Some applications of equilibrium constant are discussed below.

12.7.1 Prediction of the direction of the reaction : For the reversible reaction,

$$aA + bB \rightleftharpoons cC + dD,$$

the equilibrium constant is

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

where all concentrations are equilibrium concentrations.

The ratio is called reaction quotient, Q_C, when the concentrations are not necessarily equilibrium concentrations.

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

The reaction quotient has same form as that of equilibrium constant, but involves concentrations that are not necessarily equilibrium concentrations. Comparison of Q_C and K_C is very useful to decide whether the forward or the reverse reaction should occur to establish the equilibrium. It is shown diagramatically in Fig. 12.4.

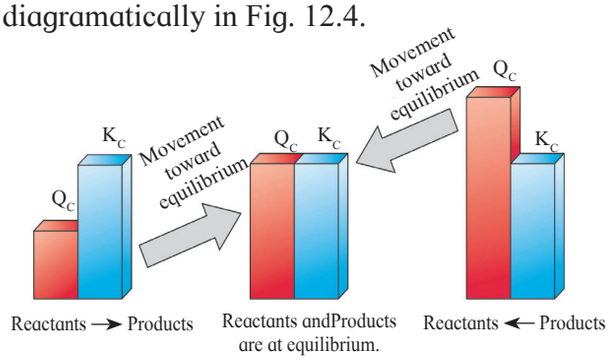


Fig. 12.4 : Predicting direction of reaction

If $Q_C < K_C$, the reaction will proceed from left to right, in forward direction, generating more product to attain the equilibrium.

If $Q_C = K_C$ the reaction is at equilibrium and hence no net reaction occurs.

If $Q_C > K_C$, the reaction will proceed from right to left, requiring more reactants to attain equilibrium.

A comparison of Q_C with K_C indicates the direction in which net reaction proceeds as the system tends to attain the equilibrium.

Note : The prediction of the direction of the reaction on the basis of Q_C and K_C values makes no comment on the time required for attaining the equilibrium.

12.7.2 : To know the extent of reaction :

Let us recall an expression for equilibrium constant K_C. (See Fig. 12.5). It indicates that the magnitude of K_C is

i. directly proportional to the equilibrium concentrations of the product.

ii. inversely proportional to the equilibrium concentrations of the reactants.

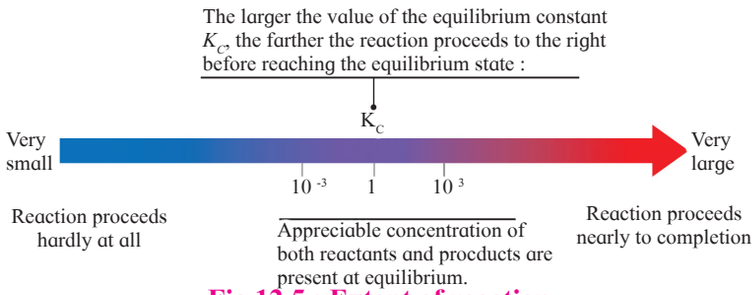


Fig 12.5 : Extent of reaction

Consider, for example, the following two reversible reactions :

$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$
Equilibrium constant values $K_C = \frac{[H_2O(g)]^2}{[H_2(g)]^2[O_2(g)]}$ $K_C = 2.4 \times 10^{47}$ At 500 K	$K_C = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(g)]^2}$ $K_C = \frac{1}{K_C} = \frac{1}{2.4 \times 10^{47}}$ $K_C = 4.1 \times 10^{-48} = 0.41 \times 10^{-47}$ at 500 K
1. Value of K_C is very high ($K_C > 10^3$).	1. Value of K_C is very low ($K_C < 10^{-3}$).
2. At equilibrium there is a high proportion of products compared to reactants.	2. At equilibrium, only a small fraction of the reactants are converted into products.
3. Forward reaction is favoured.	3. Reverse reaction is favoured.
4. Reaction is in favour of products and nearly goes to completion.	4. Reaction is in favour of reactants.
K_C >>>1. Reaction proceeds almost totally towards products.	K_C <<< 1. Rection hardly proceeds towards the products.

Can you tell?

Comment on the extent to which the forward reaction will proceed, from the magnitude of the equilibrium constant for the following reactions :

1. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_C = 20$ at 550 K
2. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$, $K_C = 10^{18}$ at 550 K

12.7.3 To calculate equilibrium concentrations : The equilibrium constant can be used to calculate the composition of an equilibrium mixture.

Consider an equilibrium reaction,

$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons$
(ethanolic acid) (ethanol)
$CH_3COOC_2H_5(aq) + H_2O(aq)$
(ethyl ethanoate)

The equilibrium constant is 4.0 at a certain temperature.

Use your brain power

The value of K_C for the dissociation reaction $H_2(g) \rightleftharpoons 2H(g)$ is 1.2×10^{-42} at 500 K
Does the equilibrium mixture contain mainly hydrogen molecules or hydrogen atoms ?

If we start with 2.0 mol of ethanoic acid and 2.0 mol of ethanol in 'V' litres. Let us find out the composition of equilibrium mixture. Consider x mol of ethyl ethanoate at equilibrium.

Internet my friend

Collect information about Chemical Equilibrium.

	$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$			
Initial (No. of moles)	2.0	2.0	0	0
At equilibrium (No. of moles)	(2.0 -x)	(2.0 -x)	x	x
Equilibrium concentrations	$\frac{(2.0 - x)}{V}$	$\frac{(2.0 - x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Equilibrium constant

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$\therefore 4.0 = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(2.0 - x)}{V} \times \frac{(2.0 - x)}{V}}$$

substituting the value of equilibrium concentration

$$\therefore 4.0 = \frac{x^2}{(2.0 - x)^2}$$

$$\therefore \sqrt{4} = \frac{x}{2.0 - x}$$

$$\therefore 2 = \frac{x}{2.0 - x}$$

$$\therefore 4 - 2x = x$$

$$\therefore x = \frac{4}{3}$$

$$\therefore x = 1.33$$

$$\therefore (2.0 - x) = 0.67$$

Therefore, equilibrium concentrations are 0.67 mol of ethanoic acid, 0.67 mol of ethanol and 1.33 mol of ethyl ethanoate in V litres.

Problem 12.5 : Equal concentrations of hydrogen and iodine are mixed together in a closed container at 700 K and allowed to come to equilibrium. If the concentraion of HI at equilibrium is 0.85 mol dm^{-3}, what are the equilibrium concentrations of H_2 and I_2 if K_C = 54 at this temperature ?

Solution : Balanced chemical reaction :

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$\therefore K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

on substituting the values

$$\therefore 54 = \frac{(0.85)^2}{[H_2(g)]^2}$$

as initial concentrations of $H_2(g)$ and $I_2(g)$ are equal.

(Refer to the balanced chemical equation : 1 mole of H_2 reacts with 1 mole of I_2)

Equilibrium concentration of I_2 (g) = Equilibrium concentration of H_2 (g)

$$\therefore 54 = \frac{(0.85)^2}{[H_2(g)]^2},$$

$$\therefore [H_2(g)] = 0.12 \text{ mol dm}^{-3}$$

Equilibrium concentrations of H_2 and I_2 are equal to 0.12 mol dm^{-3}.

12.7.4 Link between chemical equilibrium and chemical kinetics :

We have deduced in section 12.4.3

$$K_C = \frac{k_f}{k_r} \qquad \text{.....(12.7)}$$

Where k_f and k_r are velocity or **rate constants** of the forward and reverse reactions respectively. This equation can be used to determine the composition of the reaction mixture

$k_f > k_r$	$k_f \approx k_r$
$\therefore K_C$ is very large.	k_f and k_r have comparable values $\therefore K_C$ is nearly one.
$\therefore$ Reaction goes almost to completion.	Reaction never goes to completion.
$\therefore$ If k_f is much larger than K_C, the reaction may be irreversible (Reverse reaction is too slow to be detected).	Comparable concentrations of reactants and products are present at equilibrium.

Remember

The equilibrium refers to the relative amounts of reactants and products and thus a shift in equilibrium in a particular direction will imply the reaction in that direction will be favoured.

Problem 12.6 : The equilibrium constant K_C for the reaction of hydrogen with iodine is 54.0 at 700 K.

$$H_2(g) + I_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2HI(g)$$

K_C = 54.0 at 700 K

a. If k_f is the rate constant for the formation of HI and k_r is the rate constant for the decomposition of HI, deduce whether k_f is larger or smaller than k_r.

Solution : As $K_C = \frac{k_f}{k_r} = 54.0$,

k_f is greater than k_r by a factor of 54.0

b. If the value of k_r at 700 K is 1.16×10^{-3}, what is the k_f ?

$K_f = K_C \times k_r = 54.0 \times (1.16 \times 10^{-3})$

$= 62.64 \times 10^{-3}$

12.8 Le Chaterlier's principle and factors altering the composition at equilibrium :

We have learnt that a reaction attains a state of equilibrium under a certain set of conditions (temperature, pressure, concentration and catalyst).

In general, if we add more reactant, the system will react to remove it. If we remove a product, the system will react to replenish it. Under these changed conditions, new equilibrium will be established with different composition from the earlier equilibrium mixture.

The principal goal of chemical synthesis is to achieve maximum conversion of reactants to products with minimum expenditure of energy. To achieve this goal, the reaction conditions must be adjusted.

The qualitative effect of various factors on the composition of equilibrium mixture are described through the Le Chatelier's principle.

If a stress is applied to a reaction mixture at equilibrium, reaction occurs in the direction which relieves the stress. Stress means any change in concentration, pressure, volume or temperature which disturbs the original equilibrium. The direction that the reaction takes is the one that reduces the stress. For example, if concentration of the reactants is increased, reaction goes in a direction that tends to decrease the concentration, that is, in the direction of forward reaction.

Le Chatelier's Principle :

It states that, when a system at equilibrium is subjected to a change in any of the factors determining the equilibrium conditions, system will respond in such a way as to minimize the effect of change.

12.8.1 Factors affecting equilibrium :

(a) Change of concentration

Consider reversible reaction representing production of ammonia (NH_3)

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

The reaction proceeds with decrease in number of moles ($\Delta n = -2$) and the forward reaction is exothermic. Iron (containing a small quantity of molybdenum) is the catalyst.

$$\text{At equilibrium } Q_C = K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \ldots\ldots \text{(I)}$$

Stage I : system at equilibrium

Stage II : Equilibrium disturbed by making $Q_C < K_C$ by adding H_2.

Due to addition of extra hydrogen, system is no longer at equilibrium.

The system regains its equilibrium in stage III.

Stage III : Added hydrogen is to be used up and converted to more NH_3. Hence forward reaction is favoured.

Stage IV : New state of equilibrium is established.

According to Le-Chatelier's principle, the effect of addition of H_2 (or N_2 or both) is reduced by shifting the equilibrium from left to right so that the added N_2 or H_2 is consumed.

The forward reaction occurs to a large extent than the reverse reaction until the new equilibrium is established. This results in increased yield of NH_3.

Remember

In general, if the concentration of one of the species in equilibrium mixture is increased, the position of equilibrium shifts in the opposite direction so as to reduce the concentration of this species. However, the equilibrium constant remains unchanged.

(b) Effect of Pressure

You know that : Ideal gas equation is

$PV = nRT$,

On rearranging we get,

$$P = RT\frac{n}{V}$$

$\therefore P \propto \frac{n}{V}$, where the ratio $\frac{n}{V}$ is an expression for the concentration of the gas in mol dm^{-3}

1. An equilibrium mixture of dinitrogen tetroxide (colourless gas) and nitrogen dioxide (brown gas) is set up in a sealed flask at a particular temperature (refer to Fig. 12.3).

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

The effect of change of pressure on this gaseous equilibrium can be followed by observing the change in its colour intensity. See Table 12.1.

Table 12.1 : Change in colour intensity

Change in pressure	Change in colour intensity	Shift in equilibrium position
1. Decrease in pressure	The colour deepens	To the right, the side with more molecules
2. Increase in pressure	The colour lightens to almost colourless	To the left, the side with fewer molecules

In this reversible reaction, the forward reaction takes place with increase in the number of molecules, whereas reverse reaction takes place with decrease in the number of molecules.

2. Consider the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

As there is the same number of molecules of gas on both sides, change of pressure has no effect on the equilibrium. Here, there is no change in value of K_C during any change in pressure of the equilibrium reaction mixture.

Remember

A reaction in which decrease in volume takes place, reaction will be favoured by increasing pressure and the reaction with increase in volume will be favoured with lowering pressure, temperature being constant.

Remember

In a reversible reaction, the reverse reaction has an energy change that is equal and opposite to that of the forward reaction.

(c) Effect of Temperature :

Consider the equilibrium reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) + 92.5\ kJ$$

The forward reaction is exothermic. The reverse reaction is endothermic. An endothermic reaction consumes heat. Therefore, increase in temperature results in shifting the equilibrium in the reverse direction to use up the added heat (heat energy converted to chemical energy).

Now let us study the effect of change of temperature on the equilibrium constant.

1. Consider the equilibrium reaction :

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + Heat$$

$$\Delta H = -90\ kJ\ mol^{-1}$$

Equilibrium constant K_C for the reaction, is given in Table 12.2.

$$K_C = \frac{[CH_3OH\,(g)]}{[CO\,(g)][H_2\,(g)]^2}$$

Table 12.2

Temperature (K)	K_C
298	1.7×10^{17}
500	1.1×10^{11}
1000	2.1×10^{6}

The forward reaction is exothermic. According to Le Chatelier's principle an increase in temperature shifts the position of equilibrium to the left. Therefore, the concentration of $[CH_3OH(g)]$ decreases and the concentration of $CO(g)$ and $H_2(g)$ increases. $K_C = \frac{[CH_3OH(g)]}{[CO(g)][H_2(g)]^2}$

Therefore, the value of K_C decreases as the temperature is increased.

(d) Effect of Catalyst :

Rate of a chemical reaction, increases with the use of catalyst.

Consider an esterification reaction :

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons$

(ethanoic acid) (ethanol)

$CH_3COOC_2H_5(l) + H_2O(l)$

(ethyl ethanoate) (water)

If the above reaction is carried out without catalyst, it would take many days to reach equilibrium. However, the addition of hydrogen ions (H^+) as catalyst reduces the time only to a few hours.

Remember

In all the cases of change in concentration, pressure, temperature and presence of catalyst, once the equilibrium has been re-established after the change, the value of K_C will be unaltered

A catalyst does not affect equilibrium constant and equilibrium composition of a reaction mixture.

Do you know ?

Catalyst lowers activation energy for the forward and reverse reactions by exactly the same amount.

A catalyst does not appear in the balanced chemical equation and in the equilibrium constant expression.

Let us **summarize** effects of all four factors on the position of equilibrium and value of K_C.

Effect of	Position of equilibrium	Value of K_C
Concentration	Changes	No change
Pressure	Changes if reaction involves change in number of gas molecules	No change
Temperature	Changes	Changes
Catalyst	No change	No change

Making ammonia The Haber process

$$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$$

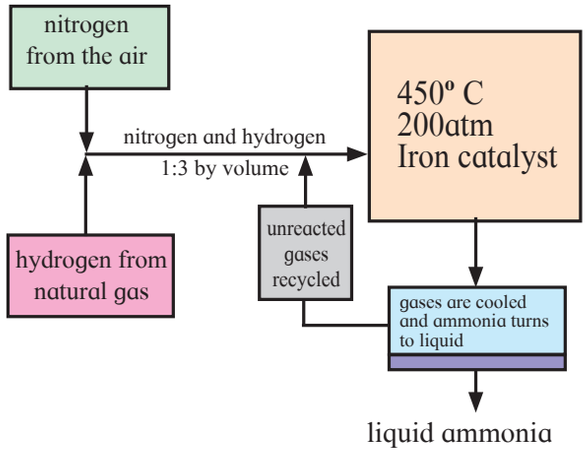


Fig. 12.6 The Haber process

12.9 Industrial Application :

The Haber process : (Industrial preparation of ammonia)

Industrial processes can be made efficient and profitable by applying ideas of rate of reaction and equilibrium.

The Haber process is the process of synthesis of ammonia gas by reacting together hydrogen gas and nitrogen gas in a particular stoichiometric ratio by volumes and at selected optimum temperature.

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

The reaction proceeds with a decrease in number of moles ($\Delta n = -2$) and the forward reaction is exothermic. Iron (containing a small quantity of molybdenum) is used as catalyst.

We studied earlier in section 12.8.1 a. how the change in concentration of the reactants affects the yield of ammonia. Now let us consider the effect of temperature and pressure on the synthesis of ammonia.

a. Effect of temperature : The formation of ammonia is exothermic reaction. Hence, lowering of temperature will shift the equilibrium to right. At low temperature however, the rate of reaction is small and longer time would be required to attain the equilibrium. At high temperatures, the reaction occurs rapidly with appreciable decomposition of ammonia. Hence, the optimum temperature has to be used. The **optimum temperature** is about 773 K.

b. Effect of pressure : The forward reaction is favoured with high pressure as it proceeds with **decrease in number of moles**. At high pressure, the catalyst becomes inefficient. Therefore optimum pressure needs to be used. The **optimum pressure is about 250 atm**.

Can you tell?

1. If NH_3 is added to the equilibrium system of Haber process, in which direction will the eqilibrium shift to consume added NH_3 so as to reduce the effect of stress?
2. In this process, out of the reverse and forward reaction, which reaction will occur to a greater extent due to this stress ?
3. What will be the effect of this stress on the yield of NH_3 ?

Internet my friend

1. Collect information about Haber Process and Chemical Equilibrium.
2. Youtube.Freesciencelessons The Haber Process.

Exercises

1. Choose the correct option

A. The equlilibrium, $H_2O(l) \rightleftharpoons H^{\oplus}(aq) + OH(aq)$ is

a. dynamic b. static
c. physical d. mechanical

B. For the equlibrium, $A \rightleftharpoons 2B$ + Heat, the number of 'A' molecules increases if
a. volume is increased
b. temperature is increased
c. catalyst is added
d. concerntration of B is decreased

C. For the equilibrium $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g)$ the concerntration of NOCl will increase if the equlibrium is disturbed by
a. adding Cl_2 b. removing NO
c. adding NOCl c. removal of Cl_2

D. The relation between K_c and K_p for the reaction $A(g) + B(g) \rightleftharpoons 2C(g) + D(g)$ is
a. $Kc = Ykp$ b. $Kp = Kc^2$
c. $Kc = \frac{1}{\sqrt{Kp}}$ d. $Kp/Kc = 1$

E. When volume of the equilibrium reaction $C(g) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ is increased at constant temperature the equilibrium will
a. shift from left to right
b. shift from right to left
c. be unaltered
d. can not be predicted

2. Answer the following

A. State Law of Mass action.

B. Write an expression for equilibrium constant with respect to concerntration.

C. Derive mathematically value of k_p for for $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

D. Write expressions of K_c for following chemical reactions

i. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
ii. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

E. Mention various applications of equilibrium constant.

F. How does the change of pressure affect the value of equilibrium constant ?

J. Differentiate irreversible and reversible reaction.

K. Write suitable conditions of concentration, temperature and pressure used during manufacture of ammonia by Haber process.

L. Relate the terms reversible reactions and dynamic equilibrium.

M. For the equilibrium.
$BaSO_4(s) \rightleftharpoons Ba^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$
state the effect of
a. Addition of $Ba^{2\oplus}$ ion.
b. Removal of $SO_4^{2\ominus}$ ion
c. Addition of $BaSO_4(s)$
on the equilibrium.

3. Explain :

A. Dynamic nature of chemical equilibrium with suitable example.

B. Relation between K_c and K_p.

C. State and explain Le Chatelier's principle with reference to
1. change in temperature
2. change in concerntration.

D. a. Reversible reaction
b. Rate of reaction

E. What is the effect of adding chloride on the position of the equilibrium ?
$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$

Activity :

Prepare concept maps of chemical equilibrium.

13. Nuclear chemistry and radioactivity

13.1 Introduction: Nuclear chemistry is a branch of physical chemistry : It is the study of reactions involving changes in atomic nuclei. This branch started with the discovery of natural radioactivity by a physicist Antoine Henri Becquerel (1852-1908). Most of the 20th century research has been directed towards understanding of the forces holding the nucleus together. To understand the changes occuring on the earth, Geologists explore nuclear reactions. Astronomers study nuclear reactions taking place in stars. In biology and medicine, the interactions of radiation emitted from nuclear reactions with the living system are important.

Examples of nuclear reactions are : radioactive decay, artificial transmutation, nuclear fission and nuclear fusion.

We briefly discuss these in this chapter. We have studied the structure of atom in Chapter 4.

13.1.1 Similarity between the solar system and structure of atom: Our solar system is made up of the Sun and planets. The Sun is at the centre of solar system and planets moving around it under the force of gravity. Analogous to this in atomic systems, the forces which hold nucleus and extranuclear electrons are attractive electrostatic.

As studied in Chapter 4, the atom consists of tiny central core called nucleus consisting of protons and neutrons and surrounding region of space being occupied by fast moving electrons.

The radius of nucleus is of the order of 10^{-15} m whereas that of the outer sphere is of the order of 10^{-10} m. The size of outer sphere, is 10^5 times larger than the nucleus. There is a large space vacant outside the nucleus.

Composition of an atom is denoted as ${}^{A}_{Z}X$ where X is the symbol of the element. Z equals number of protons and is called atomic number of the element. (Refer to chapter 4, section 4.2)

Do you know ?

How small is the nucleus in comparison to the rest of atom ?

If the atom were of the size of football stadium, the nucleus at the centre spot would be the size of a pea.

'A' is the mass number or the sum of number of protons and neutrons in an atom. N is the number of neutrons in an atom.

$$A = Z + N$$

The number of neutrons can be obtained by subtracting the atomic number, Z, from the mass number A.

The atomic number, appearing as a subscript to the left of the elemental symbol, gives the number of protons in the nucleus. The mass number written as a superscript to the left of element symbol, gives the total number of nucleons that is the sum of protons (p) and neutrons (n). The most common isotope of carbon, for example, has 12 nucleons : 6 protons and 6 neutrons,

Mass number (A) → ${}^{12}_{6}C$ ← Atomic number (Z)

Carbon 12

6 protons
6 neutrons
12 nucleons

As you know, atoms with identical atomic numbers but different mass numbers are called isotopes. The nucleus of a specific isotope is called **nuclide**.

The charge on the nucleus is $+Ze$ and that of outer sphere is $-Ze$, ('e' is the magnitude of electronic charge). The atom as a whole is, thus, electrically neutral. The mass of an electron is negligible (1/1837th of the mass of proton) in comparison to pronton or neutron. The entire mass of atom is concentrated in its nucleus. The density of nucleus is considerably higher, typically 10^5 times the density of ordinary matter.

The radius of nucleus is given by $R = R_o A^{1/3}$ where R_o is constant, common to

all nuclei and its value is 1.33 x 10^{-15} m. The volume of nucleus, $V \propto R^3$ and hence, $V \propto A$.

13.2 Classification of nuclides

13.2.1 Classification on the basis of number of nucleons : On the basis of the number of neutrons and protons constituting the nucleus, the nuclides (which refer to atomic nucleus without relation to the outer sphere) are classified as

i. Isotopes : These are nuclides which the same number of protons but different number of neutrons For example, $^{22}_{11}Na$, $^{23}_{11}Na$, $^{24}_{11}Na$. The number of neutrons in each being 11, 12 and 13, respectively.

ii. Isobars : These are nuclides which have the same mass number and different number of protons and neutrons. For example, $^{14}_{6}C$, the number of neutrons in each are 8 and 7, respectively. Likewise $^{3}_{1}H$ and $^{3}_{2}He$, or $^{14}_{6}C$ and $^{14}_{7}N$ are the pairs of isobars (Table 13.1).

Table 13.1 : Isobars

Isobars of $A = 3$	$^{3}_{1}H$ $(N = 2)$, $^{3}_{2}He$ $(N = 1)$
Isobars of $A = 14$	$^{14}_{6}C$ $(N = 8)$, $^{14}_{7}N$ $(N = 7)$
Isobars of $A = 24$	$^{24}_{11}Na$ $(N = 32)$, $^{24}_{12}Mg$ $(N=12)$

iii. Mirror nuclei : These are isobars in which the number of protons and neutrons differ by 1 and are interchanged. Examples: $^{3}_{1}H$ and $^{3}_{2}He$, $^{13}_{6}C$ and $^{13}_{7}N$

iv. Isotones : Isotones are nuclides having the same number of neutrons but different number of protons and hence, different mass numbers. For example, carbon, nitrogen, sodium, magnesium.

$^{13}_{6}C$ and $^{14}_{7}N$, $^{23}_{11}Na$ and $^{24}_{12}Mg$

v. Nuclear isomers : The nuclides with the same number of protons (Z) and neutrons (N) or the same mass number (A) which differ in energy states are called nuclear isomers. For example, ^{60m}Co and ^{60}Co. An isomer of higher energy is said to be in the meta stable state. It is indicated by writing m after the mass number.

13.2.2 Classification on the basis of nuclear stability

i. Stable nuclides : The number of electrons and the location of electrons may change in outer sphere but the number of protons and neutrons the nucleus is unchanged.

ii. Unstable or radioactive nuclides : These nuclides undergo spontaneous change in their compposition of radiation forming new nuclides.

13.3 Nuclear stability : Why are some nuclei stable while others are radioactive and undergo spontaneous change? To answer this question we need to know the factors governing stability of the nucleus.

13.3.1 Even-odd nature of proton number (Z) and neutrons (N)

Table 13.2 : Distribution of naturally occurring nuclides.

Number of protons Z	Number of neutrons N	Number of such nuclides
Even	Even	165
Even	Odd	55
Odd	Even	50
Odd	Odd	04

The distribution of naturally occuring nuclides in accordance with even/odd values of N and Z is useful to understand stability of nuclides.

a. The nuclides with the even Z and even N constitute 85% of earth crust. It indicates that nuclides with even Z and even N are stable. They tend to form proton-proton and neutron-neutron pairs and impart stability to the nucleus.

b. The number of stable nuclides with either Z or N odd is about one third of those in which both are even. This suggests that these nuclides are less stable than those having even number of protons and neutrons. In these nuclides one nucleon has no partner. Further the nuclides with odd Z or odd N are nearly the same. This indicates that protons and neutrons behave similarly in the respect of stability.

c. The stable naturally occureing nuclides with odd Z and odd N are only four. The small number is indicative of instability; which can be attributed to the presence of two unpaired

nucleons. This also indicates the separate pairing of neutrons and protons (The nucleon pairing does not take place between proton and neutron). Only 2% of the earth's crust consists of such nuclides.

13.3.2 Neutron to Proton ratio (*N/Z*) :

i. Figure 13.1 shows a plot of the neutron number (*N*) as a function of proton number (*Z*) in stable nuclides. A large number of elements have several stable isotopes. Hence, the curve appears as a belt or zone called **Stability zone**. All the stable nuclides fall within this zone. The nuclides which form outside such belt are radioactive. The straight line below the belt represents the ratio *N/Z* to be unity.

ii. As may be noticed for nuclei lighter than $^{40}_{20}Ca$, one observes the straight line (*N*=*Z*) passing through the belt. The lighter nuclides are therefore stable when their *N*/*Z* is nearly 1.

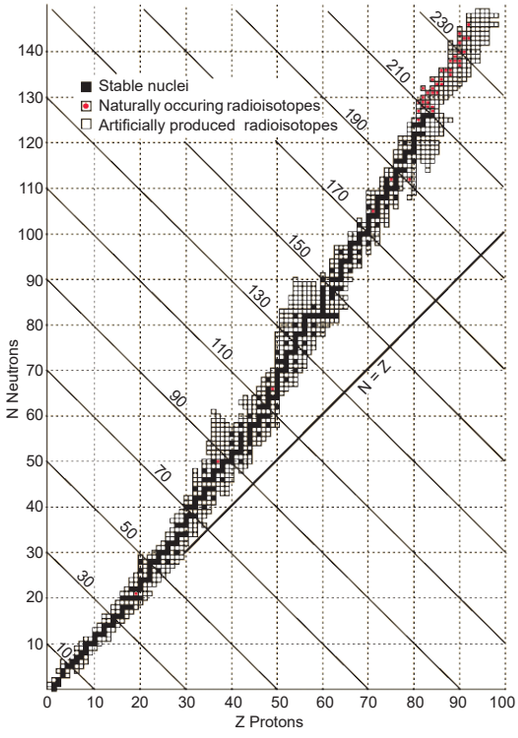


Fig. 13.1 : Neutron to Proton (*N/Z*) ratio

iii. The *N*/*Z* ratio for the stable nuclides heavier than calcium gives a curved appearance to the belt with gradually increase of *N*/*Z* (> 1). The heavier nuclides therefore, need more number of neutrons (than protons) to attain stability. What is the reason for this? The heavier nuclides with the increasing number of protons render large coulombic repulsions. With increased number of neutrons the protons within the nuclei get more separated, which renders them stable.

13.3.3 Magic numbers : The nuclei with 2, 8, 20, 28, 50, 82 and 126 neutrons or protons are particularly stable and abundant in nature. These are magic numbers. Lead ($^{208}_{82}Pb$) has two magic numbers, 82 protons and 126 neutrons.

13.3.4 Nuclear Potential : Within the nucleus, all protons are positively charged. What are the consequences of the Coulomb repulsions between these protons?

The distance between two protons present in the nucleus is typically 10^{-15} m. Obviously, the repulsion between them has to be large. If the coulomb repulsion had been the only force in operation the nucleus would not exist. However the nucleus does exist. This indicates that there are nuclear forces of attraction between all the nucleons holding them together within the nucleus. These are attractions between proton-proton, neutron-neutron and proton-neutron. These attractive forces are independent of the charge on nucleons. Hence p-p, n-n and p-n attractions are equal. These attractive forces operate over short range within the nucleus.

The p-p, n-n and p-n attractions constitute what is called the nuclear potential which is responsible for the nuclear stability.

13.3.5 Nuclear binding energy and mass defect : Binding energy of a nucleus gives a measure of how strongly nucleons are held together within the nucleus.

The energy required for holding the nucleons together within the nucleus of an atom is called as the **nuclear binding energy**. It is defined as the energy required to break the nucleus into its constituents. Here the binding of electrons to the nucleus has been neglected.

Atoms are composed of protons, neutrons and electrons. The actual mass of atom is observed to be less than sum of the masses of its constituents.

Protons and neutrons are held in a nucleus together. During the formation of nucleus, a certain mass is lost. This is known as mass defect, Δm. **An energy equivalent to the mass lost is released during the formation of nucleus. This is called the nuclear binding energy**.

In general, the exact mass of a nucleus is slightly less than sum of the exact masses of the constituent nucleons. The difference is called mass defect, **(Δm)**.

Δm = Calculated mass – Observed mass.

The conversion of mass into energy is etablished through Einstein's equation, **E = mc²**. where m is the mass of matter converted into energy E and c velocity of light.

Units of nuclear masses and energy : The nuclear mass is usually expressed in unified mass unit (u) which is exactly $1/12^{th}$ of the mass of ^{12}C atom. Thus, 1u = $1/12^{th}$ mass of C-12 atom = 1.66×10^{-27} kg.

The energy released (in Joules) in the conversion of 1 u mass into energy is given by the expression :

$E = mc^2 = (1.66 \times 10^{-27}kg) \times (3 \times 10^8 m\ s^{-1})^2$

Expression for nuclear binding energy :

Consider a nuclide ${}^{A}_{Z}X$ that contains Z protons and $(A - Z)$ neutrons. Suppose the observed mass of the nuclide is m. The mass of proton is m_p and that of neutron is m_n.

Calculated mass = $(A\text{-}Z)\ m_n + Z\ m_p + Z\ m_e$ … (13.1)

$\Delta m = [(A\text{-}Z)\ m_n + Z\ m_p + Z\ m_e] - m$

$= [(A\text{-}Z)\ m_n + Z\ (m_p + m_e)] - m$

$= [(A\text{-}Z)\ m_n + Z\ m_H] - m$ …(13.2)

where $(m_p + m_e) = m_H$ = mass of H atom.

Thus $(\Delta m) = [Zm_H + (A\text{-}Z)\ m_n] - m$

Where Z is atomic number, A is the mass number, $(A\text{-}Z)$ is neutron number, m_H and m_n are masses of hydregen atom and neutron, respectively, and m is the mass of nuclide.

The mass defect, Δm is related to binding energy of nucleus by Einstein's equation

$\Delta E = \Delta m \times c^2$

where, ΔE is the binding energy, Δm is the mass deffect. Nuclear energy is usually expressed in million electron volt (MeV), where

1 MeV = 1.602×10^{-13} J

When mass equal to in is converted into energy it is 931.4 MeV.

The total binding energy is then given by

B.E. = Δm (u) x 931.4 (MeV per u)

B.E.= $931.4(Zm_H + (A\text{-}Z)\ m_n) - m$ … (13.3)

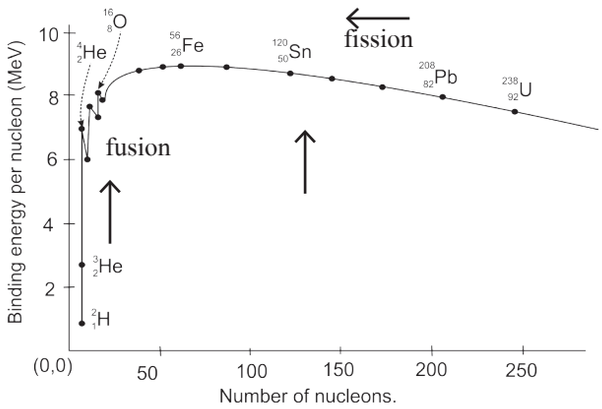


Fig. 13.2 : Binding energy per nucleon

Total binding energy of nucleus containing A number of nucleons is denoted as $B.E.$ The binding energy per nucleon is then given by,

$\bar{B} = B.E. / A$ … (13.4)

Binding energy per nucleon and nuclear stability : Mean binding energy per nucleon for the most stable isotopes as a function of mass number is shown in Fig. 13.2. This plot leads to the following inferences.

(i) Light nuclides ($A < 30$)

The peaks with A values in multiples of 4. For example, $^{4}_{2}He$, $^{12}_{6}C$, $^{16}_{8}O$ are more stable.

(ii) Medium mass nuclides : ($30 < A < 90$)

$\bar{B}$ increases typically from 8 MeV for A=16 to nearly 8.3 MeV for A between 28 and 32 and it remains nearly constant 8.5 MeV. Beyond this it shows a broad maximum. The nuclides falling on the maximum are most stable as they possess high $\bar{B}$ values. Accordingly ^{56}Fe with $\bar{B}$ value of 8.79 MeV is the most stable nuclide.

(iii) Heavy nuclides ($A > 90$)

$\bar{B}$ decreases from maximum 8.79 MeV to 7.7 MeV for $A \cong 210$, ^{209}Bi is the heaviest stable nuclide. Beyond this all nuclides are radioactive (α- emitters).

Problem : 13.1 : Calculate the mean binding energy per nucleon for the formation of $^{16}_{8}O$ nucleus. The mass of oxygen atom is 15.994 u. The masses of H atom and neutron are 1.0078 u and 1.0087 u, respectively.

Solution :

i. The mass defect, $\Delta m = Zm_H + (A - Z)\, m_n - m$

$m_H = 1.0078$ u, $m_n = 1.0087$u and $m = 15.994$ u , $Z = 8$, $A = 16$

$\Delta m = 8 \times 1.0078u + 8 \times 1.0087u - 15.994$ u $= 0.137144$ u

ii. Total binding energy, B.E. (MeV) = Δm (amu) x 931.4

Hence, B.E. = 0.137144 x 931.4 = 127.73 MeV

iii. Binding energy per nucleon, $\overline{B} = \frac{BE}{A}$

Hence, $\overline{B} = \frac{127.73 MeV}{16}$

= 7.98 MeV/nucleon

Calculate the binding energy per nucleon for the formaton of $^{4}_{2}He$ nucleus ? Mass $^{4}_{2}He$ atom = 4.0026 u.

13.4 Radioactivity : You know that some elements such as uranium and radium are radioctive elements. An element is radioactive if the nuclei of its atoms are unstable. The phenomenon in which the nuclei spontaneously emit a nuclear particle and gamma radiation transforming to a different nuclide is called radioactivity. The elements which undergo nuclear changes are radioactive elements The radioactivity is the phenomenon related to the nucleus.

The radiations emitted by radioactive elements are : alpha (α), beta (β) and gamma (Υ) radiations. Earlier you have studied the properties of α, β and Υ rays.

Try this

Prepare a chart of comparative properties of the above three types of radiations.

13.5 Radioactive decay : The probability of decay of a radioelement does not depend on state of chemical combination, temperature, pressure, presence of catalyst or even the age of nucleus.

13.5.1 Rate of decay : Rate of decay of a radioelement denotes number of nuclei of its atoms which decay in unit time. It is also called activity of radioelement.

If dN is the number of nuclei that decay within time interval dt, then rate of decay at any time t is given by

rate of decay (activity) = $-\frac{dN}{dt}$

Why is minus sign required ? The number of nuclei decreases with time. So dN is a negative quantity. However the rate of decay is a positive quantity. The negative sign is introduced in the rate expression to make the rate positive. The rate of decay is expressed as disintegrations per second (dps).

13.5.2 Rate law : The rate of decay of a radioelement at any instant is propontional to the number of nuclei (atoms) present at that instant. Thus,

$$-\frac{dN}{dt} \propto N, \text{ or } -\frac{dN}{dt} = \lambda N \qquad \ldots\ldots (13.5)$$

$$\therefore \lambda = -\frac{dN}{dt} \times \frac{1}{N}$$

where $-\frac{dN}{dt}$ being the rate of decay at any time t. N is the number of nuclei present at time t, λ the decay constant. That is the fraction of nuclei decaying in unit time.

13.5.3 Expression for decay constant :

Rearranging the Eq. (13.5)

$$\frac{dN}{N} = -\lambda\, dt$$

Integrating,

$$\int \frac{dN}{N} = -\int \lambda\, dt$$

On performing the integration, we get

$$\ln N = -\lambda t + C \qquad \ldots\ldots (13.6)$$

where C is the constant of integration whose value is obtained as follows :

Let N_0 be the number of nuclei present at some arbitrary zero time. At time t, the number of nuclei is N. So at $t = 0$, $N = N_0$. Substituting in Eq. (13.6),

$\ln N_0 = C$.

with this value of C, Eq. (13.6) becomes

$\ln N = -\lambda t + \ln N_0$

or $\lambda t = \ln N_0 - \ln N = \ln \frac{N_0}{N}$ ..... (13.7)

Hence, $\lambda = \frac{1}{t} \ln \frac{N_0}{N}$ ..... (13.8)

Converting natural logarithm (ln) to logarithm to the base 10, the eqn (13.8) becomes

$\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N}$ ..... (13.9)

The Eq. (13.7) can be expressed as $\ln \frac{N}{N_0} = -\lambda t$. Taking antilog of both sides, we get

$\frac{N}{N_0} = e^{-\lambda t}$ or $N = N_0 e^{-\lambda t}$ ..... (13.10)

The Eq. (13.9) and Eq. (13.10) give the decay constant.

13.5.4 Half life of radioelement ($t_{1/2}$) : The half life of a radioelement is the time needed for a given number of its nuclei (atoms) to decay exactly to half of its initial value. Each radio isotope has its own half life denoted by $t_{1/2}$ and expressed in seconds, minutes, hours, days or years. At any time t, number of nuclei $= N$.

At $t = 0$, $N = N_0$. Hence at $t = t_{1/2}$, $N = N_0/2$ substitution of these values of N and t in Eq. (13.9) gives

$$\lambda = \frac{2.303}{t_{1/2}} \log_{10} \frac{N_0}{N_0/2}$$

$$= \frac{2.303}{t_{1/2}} \log_{10} 2 = \frac{2.303}{t_{1/2}} \times 0.3010 = \frac{0.693}{t_{1/2}}$$

Hence, $\lambda = \frac{0.693}{t_{1/2}}$ or $t_{1/2} = \frac{0.693}{\lambda}$

13.5.5 Graphical representation of decay

i. From Eq. (13.9)

$\log_{10} N = \frac{-\lambda}{2.303} t + \log_{10} N_0$

A plot of $\log_{10} N$ versus t gives a straight line. However, $N \propto \left(-\frac{dN}{dt}\right)$. Hence, instead of $\log_{10} N$ versus t, $\log_{10}\left(-\frac{dN}{dt}\right)$ which is $\log_{10}$ (activity) is plotted versus. The graph is a straight line as shown in Fig. (13.3).

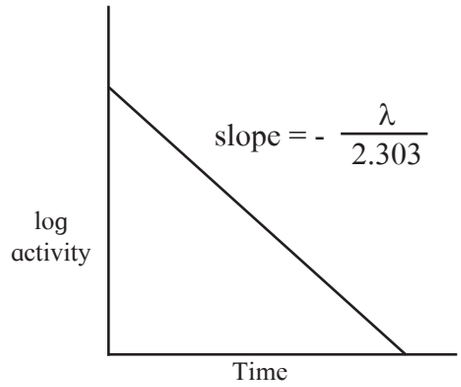


Fig. 13.3 : Plot of $\log_{10}$ activity Vs time

ii. Rate of radioactive decay at any instant is proportional to number of atoms of the radioactive element present at that instant. It is evident that as decay progresses, the number of radioactiv atoms decrease with time and so does the rate of decay. A plot of a rate or activity versus t is shown in Fig 13.4.

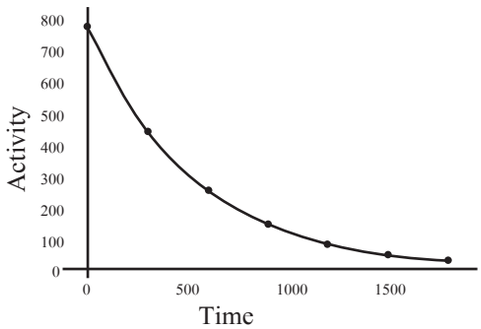


Fig. 13.4 : Plot of activity versus time

Fig. 13.4 shows a decrease in the rate of decay, that is, decrease in number of radioactive atoms with time.

Problem : 13.2

^{41}Ar decays initially at a rate of 575 Bq. The rate falls to 358 dps after 75 minutes. What is the half life of ^{41}Ar ?

Solution :

$$\lambda = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$$

where $-\frac{dN_0}{dt} = 575$ dps

$-\frac{dN}{dt} = 358$ dps and $t = 75$ min.

Hence, $\lambda = \frac{2.303}{75 \text{ min}} \log_{10} \frac{575 \text{ dps}}{358 \text{ dps}}$

$= 6.32 \times 10^{-3} \text{ min}^{-1}$

$t_{1/2} = \frac{0.693}{\lambda} = = \frac{0.693}{6.32 \times 10^{-3} \text{ min}^{-1}}$

$= 109.7$ min

Problem : 13.3

The half life of ^{32}P is 14.26 d. What percentage of ^{32}P sample will remain after 40 d?

Solution :

$$t_{1/2} = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.26 \text{ d}} = 0.0486 \text{ d}^{-1}$$

Now, $\lambda = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$

$N_0 = 100$, $N = ?$, $t = 40$ d

Hence, $\log_{10} \frac{N_0}{N} = \frac{\lambda t}{2.303}$

$= \frac{0.0486 \text{ d}^{-1} \times 40 \text{ d}}{2.303} = 0.8441$

Taking antilog of both sides we get

$\frac{N_0}{N}$ = antilog (0.8441) = 6.984

$\frac{100}{N} = 6.984$ or $N = \frac{100}{6.984} = 14.32$

% ^{32}P that remains after 40 d = 14.32 %

Problem : 13.4

The half life of ^{34}Cl is 1.53 s. How long does it take for 99.9 % of sample of ^{34}Cl to decay?

Solution :

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.53 \text{s}} = 0.453 \text{ s}^{-1}$$

Now, $\lambda = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$

$N_0 = 100$, $N = 100 - 99.9 = 0.1$, $t = ?$

Hence, $0.453 \text{ s}^{-1} = \frac{2.303}{t} \log_{10} \frac{100}{0.1}$

or $t = \frac{2.303}{0.453 \text{ s}^{-1}} \times \log_{10}(1000)$

$= \frac{2.303}{0.453 \text{ s}^{-1}} \times 3 = 15.25$ s

Problem : 13.5

The half life of $^{209}P_0$ is 102 y. How much of 1 mg sample of polonium decays in 62 y?

Solution :

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{102 \text{ y}} = 6.794 \times 10^{-3} \text{ y}^{-1}$$

$\lambda = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$

Hence, $\log_{10}\left(\frac{N_0}{N}\right) = \frac{\lambda t}{2.303}$

or, $\log_{10}\left(\frac{N_0}{N}\right)$

$= \frac{6.794 \times 10^{-3} \text{ y}^{-1} \times 62 \text{ y}}{2.303} = 0.1829$

It then follows that

$\frac{N_0}{N}$ = antilog (0.1829) = 1.524

$N = \frac{N_0}{1.524} = \frac{1 \text{ mg}}{1.524} = 0.656$ mg

N the amount that remains after 62 y. Hence, the amount decayed in

62 y = 1 mg - 0.656 mg = 0.344 mg

13.5.6 Units of radioactivity : Rate of radioactive decay is expressed in dps. The unit for the radioactivity is curie (Ci).

1 Ci = 3.7 x 10^{10} dps (disintegrations per second)

Another unit of radioactivity is Becquerel (Bq)

1 Bq = 1 dps. Thus, 1Ci = 3.7 x 10^{10} dps = 3.7 x 10^{10} Bq

13.6 Modes of decay : Radioelements decay by 3 ways, namely, α- decay, β- decay and γ- emission.

13.6.1 Alpha decay : The emission of ∝- particle from the nuclei is called ∝- decay. You have learnt that the charge of an ∝- particle is +2 and its mass is 4 u. It is identical with helium nucleus and hence an ∝- particle is also designated as $^{4}_{2}He$.

In the ∝- decay process, the parent nucleus $^{A}_{z}X$ emits an α- particle and produces daughter nucleus Y. The parent nucleus thus loses two protons (charge +2) and two neutrons. The total mass lost is 4 u. The daughter nucleus will, therefore, have mass 4 units less and charge 2 units less than its parent. The ∝- decay process is, then, written as a general equation :

$$^{A}_{z}X \longrightarrow {}^{A-4}_{z-2}Y + {}^{4}_{2}He$$

parent Daughter emitted particle

For example,

Radium 226 decays to form Radium 222 :

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

parent Daughter emitted particle

Uranium 238 decays to give Thorium 234 :

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

parent Daughter emitted particle

Note that in ∝- decay, the daughter nucleus formed belongs to an element that occupies two places to the left of the periodic table.

13.6.2 β- decay : β^- - decay : The emission of negatively charged stream of β^- particles from the nucleus is called β^- - decay. You know that β^- - particles are electrons with a charge and mass of an electron, mass being negligible as compared to the nuclei. A nucleus decays by emitting a high speed electron called a beta particle (β). A new daughter nucleus is formed with the same mass number as the original parent nucleus but an atomic number that is one unit greater.

$$^{A}_{z}X \longrightarrow {}^{A}_{z+1}Y + {}^{0}_{-1}e$$

parent Daughter emitted particle

Note that the mass number A does not change, the atomic number changes. Examples of beta decay :

Neptunium 238 decays to form plutonium 238:

$$^{238}_{93}Np \longrightarrow {}^{238}_{94}Pu + {}^{0}_{-1}e$$

parent Daughter emitted particle

Plutonium 241 decays to form americium 241:

$$^{241}_{94}Pu \longrightarrow {}^{241}_{95}Am + {}^{0}_{-1}e$$

parent Daughter emitted particle

13.6.3 γ - decay : γ-Radiation is almost always accompanied with α and β^- decay processes. In α and β^- decay process, the daughter nucleus formed is in energetically excited state. Ground state product are formed with emission of γ - rays.

For example, $^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He + \gamma$

$^{238}_{92}U$ emits α-particles of two different energies, 4.147 MeV (23%) and 4.195 MeV (77%). When α- particles of energy 4.147 MeV are emitted, ^{234}Th is left in an excited state which de-excites to the ground state with emission of γ- ray photons energy 0.048 MeV.

13.7 Nuclear reactions : We have so far discussed natural (spontaneous) nuclear rections through α and β- decay processes. Now we consider the non-spontaneous (man-made) nuclear reactions or nuclear transmutations.

13.7.1 Transmutation : The nuclear transmutation is transformation of a stable nucleus into another nucleus be it stable or unstable. The nuclear transmutation where the product nucleus is radioactive is called artificial radioactivity.

Table 13.3 : Comparison of chemical reactions and nuclear reactions

Chemical Reactions	Nuclear Reactions
1. Rearrangement of atoms by breaking and forming of chemical bonds.	1. Elements or isotopes of one elements are converted into another element in a nuclear reaction.
2. Different isotopes of an element have same behaviour.	2. Isotopes of an element behave differently.

3. Only outer shell electrons take part in the chemical reaction.	3. In addition to electrons, protons, neutrons, other elementary particles may be involved.
4. The chemical reaction is accompanied by relatively small amounts of energy. e.g. chemical combustion of 1.0 g methane releases only 56 kJ energy.	4. The nuclear reaction is accompanied by a large amount of energy change. e.g. The nuclear transformation of 1 g of Uranium - 235 releases 8.2×10^7 kJ
5. The rates of reaction is influenced by the temperature, pressure, concentration and catalyst.	5. The rate of nuclear reactions are unaffected by temperature, pressure and catalyst.

13.7.2 Induced or artificial radioactivity :

It is type of nuclear transmutation in which the stable nucleus is converted into radioactive nucleus. The product nucleus decays spontaneously with emission of radiation and particles. For example, the stable element ^{10}B, when bombarded with α- particles, transforms into ^{13}N which spontaneously emits positrons.

$$^{10}_{5}B + {}^{4}_{2}He \longrightarrow {}^{13}_{7}N + {}^{1}_{0}n \ ,$$

$$^{13}_{7}N \longrightarrow {}^{13}_{6}C + {}^{0}_{1}e$$

stable Radioactive

(spontaneous emission of positron)

Try this

^{24}Mg and ^{27}Al, both undergo (α,n) reactions and the products are radioactive. These emit β particles having positive charge (called positrons). Write balanced nulcear reactions in both.

13.7.3 Nuclear fission : Nuclear fission is splitting of the heavy nucleus of an atom into two nearly equal fragments accompanied by release of the large amount of energy. When a uranium nucleus absorbs neutron, it breaks and releases energy (Heat), more neutrons, and other radiation.

For example, ^{235}U nucleus captures neutrons and splits into two lighter fragments.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{142}_{56}Ba + {}^{91}_{36}Kr + 3\,{}^{1}_{0}n + \text{Energy}$$

Each fission may lead to different products. The mass of the fission products is less than the parent nucleus. A large amount of energy corresponding to the mass loss is released in each fission. When one Uranium 235 nucleus undergoes fission, three neutrons are emitted, which subsequently disintegrate three more Uranium nuclei and thereby produce nine neutrons. Such a chain continues by itself. In a very short time enormous amount of energy is liberated, which can be utilized for destructive (dangerous explosives) or peaceful purposes (nuclear reactor - Power Plant).

There is no unique way for fission of ^{235}U that produces Ba and Kr, and 400 ways for fission of ^{235}U leding to 800 fission products are known. Many of these are radioactive which undergo spontaneous disintegrations giving rise to new elements in the periodic table.

Interestingly each fission emits 2 to 3 neutrons (on an average 2.5 neutrons). Can you imagine what will happen due to neutron emission? Obviously these neutrons emitted in fission cause more fission of the uranium nuclei which yield more neutrons. These neutrons again bring forth fission producing further neutrons. The process continues indefinitely leading to chain reaction which continues even after the removal of bombarding neutrons. Energy released per fission is ~ 200 MeV.

Do you know ?

The chain reaction in fission of ^{235}U becomes self sustaining. What is the critical mass of ^{235}U ?

The chain reaction occurs so rapidly that nuclear explosion results. This is what happens in atom bomb.

13.7.5 Nuclear fusion : Energy received by earth from the Sun is the result of nuclear fusion. In the process, the lighter nuclei combine (fuse) together and form a heavy nucleus which is accompanied by an enormous amount of energy. Representative fusion reactions occuring in the Sun and stars are

i. $_{1}^{1}H + _{1}^{1}H \longrightarrow {}_{1}^{2}H + {}_{-1}^{0}e$

ii. $_{1}^{1}H + _{1}^{2}H \longrightarrow {}_{2}^{3}He$

iii. $_{2}^{3}He + _{2}^{3}He \longrightarrow {}_{2}^{4}He + 2\,{}_{1}^{1}H$

iv. $_{2}^{3}He + _{1}^{1}H \longrightarrow {}_{2}^{4}He + {}_{1}^{0}e$

Problem : 13.6

How many α and β- particles are emitted in the following ?

$_{93}^{237}Np \longrightarrow {}_{83}^{209}Bi$

Solution : The emission of one α - particle decreases the mass number by 4 whereas the emission of β- particles has no effect on mass number.

Net decrease in mass number = 237 - 209 = 28. This decrease is only due to α- particles.

Hence number of α- particles emitted

$= \frac{28}{4} = 7$

Now the emission of one α-particle decreases the atomic number by 2 and β-particle emission increases by 1.

The net decrease in atomic number = 93 - 83 = 10

The emission of 7 α-particles causes decrease in atomic number by 14. However the actual decrease is only 10. It means atomic number increses by 4. This increase is due to emission of β-particles. Thus, 4 β- particles are emitted.

Problem : 13.7

Estimate the energy released in the fusion reaction

$_{1}^{2}H + _{2}^{3}He \longrightarrow {}_{2}^{4}He + {}_{1}^{1}H$

Given atomic masses : $^{2}H = 2.041$ u

$^{3}He = 3.0160$ u, $^{4}He = 4.0026$ u, $^{1}H = 1.0078$ u

Solution :

Mass defect Δm = (mass of ^{2}H + mass of ^{3}He) - (mass of ^{4}He + mass of ^{1}H)

= 2.0141 u + 3.0160 u - 4.0026 u - 1.0078 u = 0.0197 u.

E = Δm (u) x 931.4 = 0.197 u x 931.4 = 18.35 MeV.

Problem : 13.8

Half life of ^{209}Po is 102 y. How many α-particles are emitted in 1s from 2 mg sample of Po?

Solution :

Activity = number of α (or β) particles emitted

$$= -\frac{dN}{dt} = \lambda N$$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{(102 \times 365 \times 24 \times 3600)s}$$

$= 2.154 \times 10^{-10}\ s^{-1}$.

$$N = \frac{2 \times 10^{-3} \times 6.022 \times 10^{23}}{209}$$

$= 5.763 \times 10^{18}$ atoms of nuclei

$$= -\frac{dN}{dt} = \lambda N$$

$= 2.154 \times 10^{-10} s^{-1} \times 5.763 \times 10^{12}$ atoms

$= 1241$ particles s^{-1}.

Nuclear fusion has certain advantages over nuclear fission. Fusion produces relatively more energy per given mass of fuel.

The only difficulty with fusion is it requires extremely high temperature typically 10^{8} K.

13.8 Applications of Radio isotopes

13.8.1 Radiocarbon dating : The technique is used to find the age of historic and archaelogical organic samples such as old wood samples and animal or human fossils.

i. Radioactive ^{14}C is formed in the upper atmosphere by bombarment of neutrons from cosmic rays on ^{14}N.

$_{7}^{14}N + _{0}^{1}n \longrightarrow {}_{6}^{14}C + {}_{1}^{1}H$

ii. ^{14}C combines with atmospheric oxygen to form $^{14}CO_2$ which mixes with ordinary $^{12}CO_2$.

iii. Carbon di oxide is absorbed by plants during photosynthesis. Animals eat plants. Hence, ^{14}C becomes a part of plant and animal bodies.

Do you know ?

The oldest rock found so far in Northern Canada is 3.96 billion years old.

iv. As long as plant is alive, the ratio $^{14}C/^{12}C$ remains constant. When the plant dies, photosynthesis occurs no more and the ratio $^{14}C/^{12}C$ decreases with the decay of ^{14}C (half life 5730 years).

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

Activity :

You have learnt in Std. 9th, medical, industrial and agricultural applications of radioisotopes. Write at least two applications each.

v. The activity (N) of given wood sample and that of fresh sample of live plant (N_0) is measured. N_0 denotes, the activity of the given sample at the time of death.

vi. The age of the given wood sample, rather the period over which it has remained dead can be determined.

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

where $\lambda = \frac{0.693}{5730\ y} = 1.21 \times 10^{-4}\ y^{-1}$.

13.8.2 Electrical energy from Nuclear fission

Do you know what is the Nuclear Power ?

It is simply the electricity made from fission of uranium and plutonium.

Why should we care about the Nuclear power?

a. It offers huge environmental benefits in producing electricity.

b. It releases zero carbon dioxide.

c. It releases zero sulfur and nitrogen oxides. These are atmospheric pollutants which pollute the air. Thus it is a clean energy.

We are intersted in Nuclear power because :

Fission of 1 gram of uranium-235 produces about 24,000 kW/h of energy.

This is the same as burning 3 tons of coal or 12 barrels of oil, or nearly 5000 m^3 of natural gas.

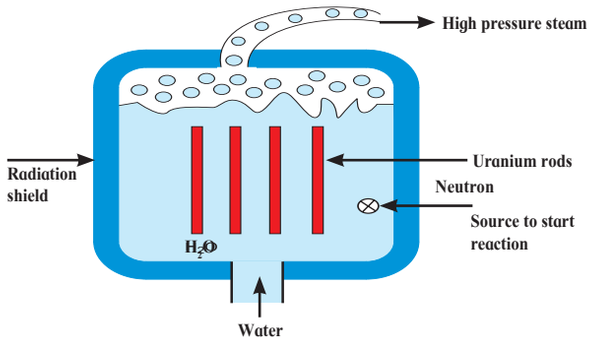


Fig. 13.4 (a) : simplified nuclear reactor

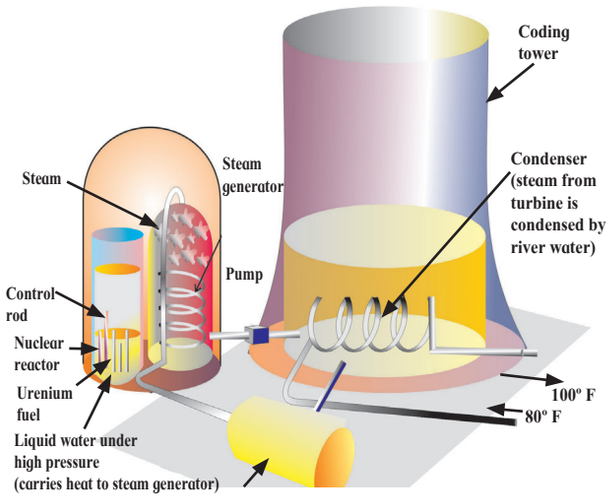


Fig. 13.4 (b) : Schematic diagram of nuclear power plant

The nuclear fission is an alternative enegy source. Traditionally, the steam comes from boilers fuelled by oil, gas, or coal. **These sources are depleting. The increasing costs of petroleum suggest we need to depend on the nuclear fission energy for electricity.**

Nuclear Reactor : Nuclear reactor is a device for using atomic energy in controlled manner for peaceful purposes. During nuclear fission energy is released. The released energy can be utilized to generate electricity in a nuclear reactor.

In a nuclear reactor, U^{235} or P^{239}, a fissionable material is stacked with heavy water (D_2O Deuterium oxide) or graphite called moderator. The neutrons produced in the fission pass through the moderator and lose a part of their energy. Subsequently the slow neutrons are captured which initiate new fission.

Table 13.4 (a) : Diagnostic Radioisotopes

	Isotope	Half-life	Emitted particles	Uses
(i) $^{51}_{24}Cr$	Chromium-51	28 days	gamma	spleen imaging
(ii) $^{59}_{26}Fe$	Iron-59	45 days	beta, gamma	bone marrow function

Table 13.4 (b) : Therapeutic Radioisotopes

	Isotope	Half-life	Emitted particles	Uses
(i) $^{35}_{15}P$	phosphours-32	14 days	beta	treatment of leukemia
(ii) $^{60}_{27}Co$	cobalt-60	5.3 years	beta, gamma	external radiation source for cancer treatment
(iii) $^{131}_{53}I$	iodine-131	8 days	beta, gamma	treatment of thyroid cancer
(iv) $^{226}_{88}Ra$	radium- 226	1620 years	beta, gamma	implanted in tumours

Cadmium rods are inserted in the moderator and they have ability to absorb neutrons. The rate of chain reaction thus is controlled. The energy released in such reaction appears as heat and removed by circulating a liquid (coolant). The coolant which has absorbed excess of heat from the reactor is passed over a heat exchanger for producing steam, which is then passed through the turbines to produce electricity. **Thus, the atomic energy produced with the use of fission reaction can be controlled in the nuclear reactor explored for peaceful purposes such as conversion into electrical energy generating power for civilian purposes, ships, submarines etc.**

13.8.3 Applications in medicine :

Hospitals and larger medical clinics typically have a Department of Nuclear Medicine.

Several radioisotopes are used for the treatment of fatal diseases like Cancer.

Table shows medical uses in two different categories, namely diagnostic and therapeutic. For diagnostic purpose, short-lived isotopes are used to limit the exposure time to radiation, while therapeutic radioisotopes are used to destroy abnormal, usually Cancerous cells.

13.8.4 Other applications of radioisotopes :

Radioisotopes find a variety of applications in the diverse areas Agricultural products those are preserved by irradiating with gamma rays from Cobalt - 60 or Caesium - 137.

Another application is radio-tracer technique wherein one or more atoms of a chemical compound are replaced by a radionuclide to trace the path followed by that chemical in the system under study by radioactivity measurement.

Do you know ?

Bhabha Atomic Research Centre (BARC) Mumbai has set up irradiation plants for preservation of agricultural produce such as mangoes, onion and potatoes at Vashi (Navi Mumbai) and Lasalgaon (Nashik).

Internet my friend

1. Isotopic tracer technique : www.iaea.org>topics>radiotracers
2. Collect information about Nuclear Reactions.

Exercises

1. Choose correct option.

A. Identify nuclear fusion reaction

a. $^{1}_{1}H + {}^{1}_{1}H \longrightarrow {}^{2}_{1}H + {}^{0}_{1}e$

b. $^{2}_{1}H + {}^{1}_{1}H \longrightarrow {}^{3}_{2}He$

c. $^{3}_{1}H + {}^{1}_{1}H \longrightarrow {}^{3}_{1}H + {}^{1}_{1}p$

B. The missing particle from the nuclear reaction is

$^{27}_{13}Al + {}^{4}_{2}He \longrightarrow ? + {}^{1}_{0}n$

a. $^{30}_{15}P$ b. $^{32}_{16}S$ c. $^{14}_{10}Ne$ d. $_{14}Si$

C. $^{60}_{27}CO$ decays with half-life of 5.27 years to produce $^{60}_{28}Ni$. What is the decay constant for such radioactive disintegration ?

a. 0.132 y^{-1} b. 0.138 c. 29.6 y d. 13.8%

D. The radioactive isotope used in the treatment of Leukemia is

a. ^{60}Co b. ^{226}Ra

c. ^{32}P d. ^{226}I

E. The process by which nuclei having low masses are united to form nuclei with large masses is

a. chemical reaction

b. nuclear fission

c. nuclear fusion

d. chain reaction

2. Explain

A. On the basis of even-odd of protons and neutrons, what type of nuclides are most stable ?

B. Explain in brief, nuclear fission.

C. The nuclides with odd number of both protons and neutrons are the least stable. Why ?

D. Referring the stabilty belt of stable nuclides, which nuclides are β^- and β^+ emitters ? Why ?

E. Explain with an example each nuclear transmutation and artifiacial radioactivity. What is the difference between them ?

F. What is binding energy per nucleon ? Explain with the help of diagram how binding energy per nucleon affects nuclear stability ?

G. Explain with example α - decay.

H. Energy produced in nuclear fusion is much larger than that produced in nuclear fission. Why is it difficult to use fusion to produce energy ?

I. How does *N/Z* ratio affect the nuclear stability ? Explain with a suitable diagram.

J. You are given a very old sample of wood. How will you determine its age ?

3. Answer the following question

A. Give example of mirror nuclei.

B. Balance the nuclear reaction:

$^{118}_{54}Xe \longrightarrow ? + {}^{118}_{54}I$

C. Name the most stable nluclide known. Write two factors responsible for its stability.

D. Write relation between decay constant of a radioelement and its half life.

E. What is the difference between an α - particle and helium atom ?

F. Write one point that differentiates nuclear reations from chemical reactions.

G. Write pairs of isotones and one pair of mirror nuclei from the following :

$^{10}_{5}B$, $^{12}_{6}C$, $^{27}_{13}Al$, $^{11}_{6}C$, $^{28}_{14}S$:

H. Derive the relationship between half life and decay constant of a radioelement.

I. Represent graphically $\log_{10}$ (activity / dps) versus t/s. What is its slope ?

J. Write two units of radioactivity. How are they interrelated ?

K. Half life of ^{24}Na is 900 minutes. What is its decay constant?

L. Decay constant of ^{197}Hg is 0.017 h^{-1}. What is its half life ?

M. The total binding energy of ^{58}Ni is 508 MeV. What is its binding energy per nucleon ?

N. Atomic mass of $^{32}_{16}S$ is 31.97 u. If masses of neutron and H atom are 1.0087 u and 1.0078 u respectively. What is the mass defect ?

O. Write the fusion reactions occuring in the Sun and stars.

P. How many α and β - particles are emitted in the trasmutation

$^{232}_{90}Th \longrightarrow {}^{208}_{82}Pb$?

Q. A produces B by ∝- emission. If B is in the group 16 of periodic table, what is the group of A ?

R. Find the number of α and β- particles emitted in the process

$^{222}_{86}Rn \longrightarrow {}^{214}_{84}Po$

4. Solve the problems

A. Half life of ^{18}F is 110 minutes. What fraction of ^{18}F sample decays in 20 minutes ?

(Ans. : 0.118)

B. Half life of ^{35}S is 87.8 d. What percentage of ^{35}S sample remains after 180 d ?

(Ans. : 24.2%)

C. Half life ^{67}Ga is 78 h. How long will it take to decay 12% of sample of Ga ?

(Ans.14.44)

D. 0.5 g Sample of ^{201}Tl decays to 0.0788 g in 8 days. What is its half life ?

(Ans.3.0 d)

E. 65% of ^{111}In sample decays in 4.2 d. What is its half life ?

(Ans. : 2.77 d)

F. Calculate the binding energy per nucleon of $^{84}_{36}Kr$ whose atomic mass is 83.913 u. (Mass of neutron is 1.0087 u and that of H atom is 1.0078 u).

(Ans.: 8.7 MeV)

G. Calculate the energy in Mev released in the nuclear reaction

$^{174}_{77}Ir \longrightarrow {}^{170}_{75}Re + {}^{4}_{2}He$

Atomic masses : Ir = 173.97 u,
Re = 169.96 u and
He = 4.0026 u

(Ans.6.89 MeV)

H. A 3/4 of the original amount of radioisotope decays in 60 minutes. What is its half life ?

(Ans.: 30 min)

I. How many - particles are emitted by 0.1 g of ^{226}Ra in one year?

(Ans. : 1.154×10^{17})

J. A sample of ^{32}P initially shows activity of one Curie. After 303 days the activity falls to 1.5×10^4 dps. What is the half life of ^{32}P ?

(Ans.14.27 d)

K. Half life of radon is 3.82 d. By what time would 99.9 % of radon will be decayed.

(Ans.38.05 d)

L. It has been found that the Sun's mass loss is 4.34×10^9 kg per second. How much energy per second would be radiated into space by the Sun ?

(Ans.: 3.9×10^{23} kJ/s)

M. A sample of old wood shows 7.0 dps/g. If the fresh sample of tree shows 16.0 dps/g, How old is the given sample of wood ? Half life of ^{14}C 5730 y.

(Ans. 6833 g)

Activity :

1. Discuss five applications of radioactivity for peaceful purpose.

2. Organize a trip ot Bhabha Atomic Reasearch Centre, Mumbai to learn about nuclear reactor. This will have to be organized through your college.

14. Basic Principles of Organic Chemistry

Can you recall?

- Which is the essential element in all organic compounds ?
- What is the unique property of carbon that makes organic chemistry a separate branch of chemsitry?
- Which classes of organic compounds are often used in our daily diet ?

14.1 Introduction : Of all the elements, only carbon is able to form an immense array of compounds, ranging from methane having one carbon atom to deoxyribonucleic acid (DNA) with billions of carbon atoms. Crude oil is a complex mixture of compounds called hydrocarbons. The pharmaceutical industry is one of the most important chemical industries that provides us medicines which are organic compounds. We need to study the organic compounds for they are interesting in their own right and their functions are greatly important to life.

Try this

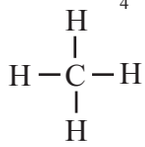
Find out the structures of glucose, vanillin, camphor and paracetamol using internet. Mark the carbon atoms present in them. Assign the hybridization state to each of the carbon and oxygen atom. Identify sigma (σ) and pi (π) bonds in these molecules.

14.2 Structural Representation of organic molecules

Try this

- Draw the structural formula of ethane.
- Draw electron-dot structure of propane.

In the previous standards you learnt how to write structural formulae and electron dot structure of hydrocarbons. Structural formula of a molecule shows all the constituent atoms denoted with their symbols and all covalent bonds therein represented by a dash joining mutually bonded atoms. For example, structural formula of CH_4 is :



In the electron dot structures of molecules, the valence electrons of all the atoms are shown as dots around them. Two dots drawn in between two atoms indicate one covalent bond between them. For example, the electron dot structure of methane is as shown here

Electron dot structures are called Lewis structures and the dash formula represents simplified Lewis formula. Chemists have developed some more ways to represent organic molecules fulfilling specific requirements.

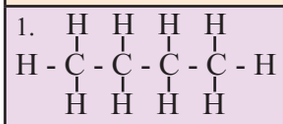
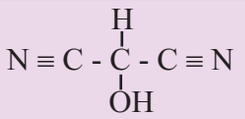
14.2.1 Condensed formula : The complete structural formula can be further simplified with hiding of some or all the covalent bonds and indicating the number of identical groups attached to an atom by a subscript. The resulting formula of a compound is known as **condensed formula**. For example : condensed formula of ethane can be written as CH_3 - CH_3 or CH_3CH_3.

14.2.2 Bond line formula or zig-zag formula

In this representation of a molecule symbols of carbon and hydrogen atoms are not written. The lines representing carbon-carbon bonds are drawn in a zig-zag manner and the terminals of the zig-zag line represent methyl groups. The intersection of lines denotes a carbon atom bonded to appropriate number of hydrogen which satisfy the tetravalency of carbon atoms. For example : propane is represented by the zig-zag formula  . However the heteroatoms or hydrogen atoms bonded to heteroatoms are written clearly. For example : The bond line formula of C_2H_5OH is  OH.

Try this Complete the Table 14.1

Table 14.1 : Representation of structural formula

Dash formula	Condensed formula A	Condensed formula B	Bond line or zig-zag formula
1. 	$CH_3(CH_2)_2CH_3$	CH_3- CH_2 - CH_2- CH_3	
2.	.....	.....	
3.	$CH_3(CH_2)_2CHO$	.....	.....
4.	$CH_3CH_2CH(CH_3)OH$	.....	.....
5. 	.....	.....	.....

14.2.3 Drawing the molecules in three dimensions : Most organic molecules have three dimensional shapes. Four different methods are used to represent three dimensional molecules on plane paper.

I. Wedge formula : The three dimensionl (3-D) view of a molecule can be represented on plane paper by representing the single bonds using solid wedge (▬), dashed wedges (|||||||||) and normal line (–). A solid wedge is used to represent a bond projecting up from the paper towards the reader. A dashed wedge is used to represent a bond going backward, below the paper away from the reader. Normal lines depict bonds in the plane of the paper. See Fig. 14.1 (for convenience solid and dashed wedge can be replaced by solid/bold and dashed lines.)

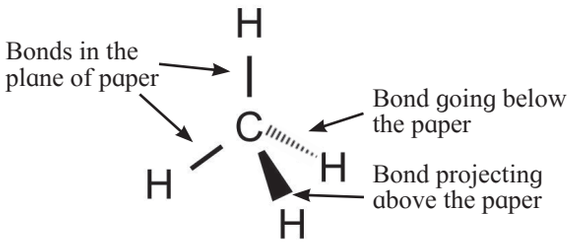


Fig. 14.1 : Wedge formula

II. Fischer projection formula or cross formula : In this representation a three dimensional molecule is projected on plane of paper. A Fischer projection formula can be drawn by visualizing the molecule with its main carbon chain vertical. Each carbon on the vertical chain is represented by a cross. The convention is that the horizontal lines of the cross represent bonds projecting up from the carbon and the vertical lines represent the bonds going below the carbon. Figure 14.2 illustrates the conventions of Fischer projection formula.

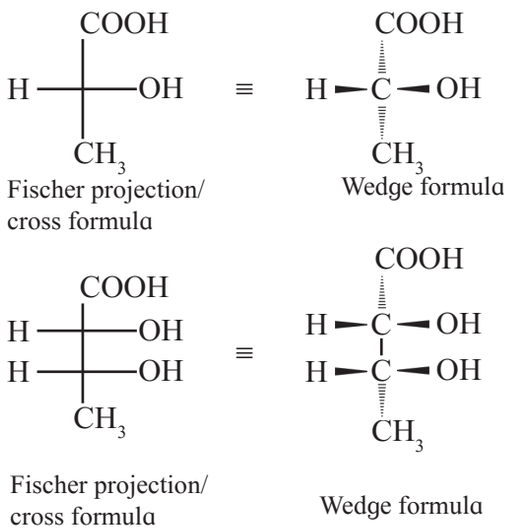
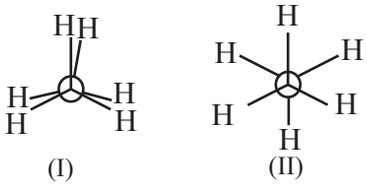


Fig 14.2 : Fischer projection (cross) formula

Fischer projection formula is more commonly used in carbohydrate chemistry

III Newman projection formula : In this method projection of a three dimensional molecule on the plane of the paper is drawn by visualizing the molecule by looking through a

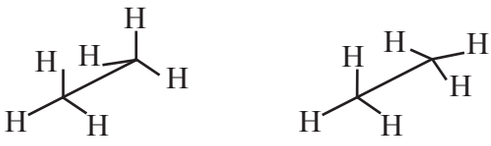
C-C single bond. In such case the C-C is not visible. A convention is followed to represent the front carbon by a point and the rear carbon by a circle around it. The remaining three bonds at each of these two carbons are drawn like spokes of a wheel. Conventionally three bonds at the front carbon are shown to radiate from the centre of the circle (which is the front carbon) and three bonds at the rear carbon are shown to radiate from the circumference of the circle. Figure 14.3 shows two representations of ethane (CH_3-CH_3) molecule by this method.



(I) (II)

Fig 14.3 : Newman projection formula of ethane

IV. Sawhorse or andiron or perspective formula : In this representation a C-C single bond is represented by a long slanting line. The lower end of the line represents the front carbn and the upper end the rear carbon. The remaining three bonds at the two carbons are shown to radiate from the respective carbons. (As the central C-C bond is drawn rather elongated the bonds radiating from the front and rear carbons do not intermingle.) Figure 14.4 shows two sawhorse (i.e. andiron or pesrpective) formulae for ethane.



(I) (II)

Fig. 14.4 : Sawhorse formula of ethane

Try this

Draw two Newman projection formulae and two sawhorse formulae for the propane molecule.

14.3 Classification of organic compounds :

With so many different molecules to study, it is important to find ways of relating different structures of molecules to their chemical properties. This provides basis for classifying organic compounds. Organic compounds are broadly classified in two ways, on the basis of (i) carbon skeleton and (ii) functional group.

Do you know ?

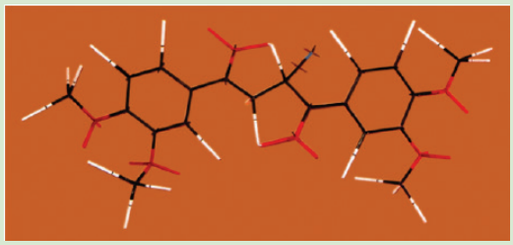
Molecular models (Fig 14.5) are used for an easier visualisation of three dimensional shapes of organic molecules. Three types of molecular models are common.

i. Frame work model : It emphasizes the skeletal pattern of bonds ignoring size of atoms.

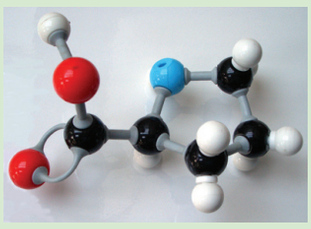
ii. Ball and stick model : In this model a ball represents an atom and stick a bond.

iii. Space filling model : It emphasizes on relative size of each atom. Bonds are not shown. It conveys volume occupied by each atom in the molecule.

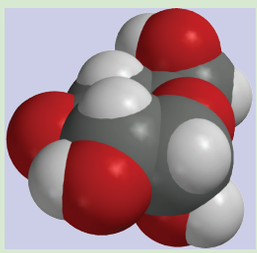
Now a days computer graphics can be used for molecular modeling.



(a) Framework model



(b) Ball and stick model



(c) Space filling model

Fig. 14.5 Molecular models

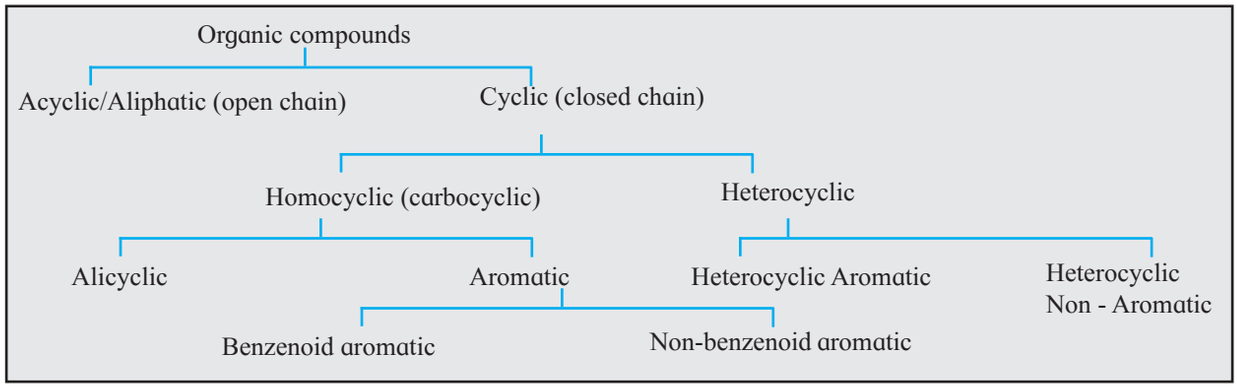


Fig 14.6 : Tree of classification of organic compounds

14.3.1 Classification based on carbon skeleton

Try this

Construct a model of propane (C_3H_8) molecule. Which atoms are on the surface of the molecule ? Which atoms lie in the core of the molecule ?

The carbon atoms bonded to each other lie in the core of an organic molecule and are described as the carbon skeleton of the molecule. It is the carbon skeleton of a molecule that decides its shape and size. A variety of carbon skeleton are found in different organic compounds and accordingly they are classified into various types as shown in Fig. 14.6

Acyclic or open chain compounds : These are also known as **aliphatic compounds**. Molecules of these compounds have chains of carbon atoms. These may be straight chains formed by carbon atoms bonded to one or two other carbons or branched chains having at least one carbon bonded to three or four other carbons. Table 14.2 shows examples of acyclic compounds.

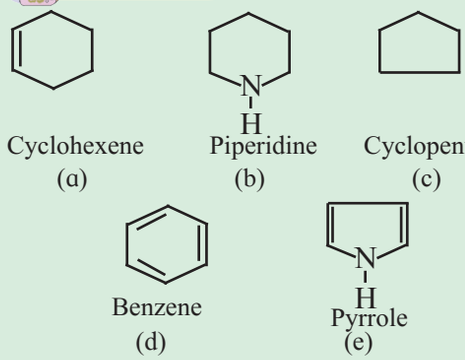
Table 14.2 : Acyclic/Aliphatic compounds

CH_3- CH_2 - CH_3 propane	CH_3- CH_2 - CH_2 - OH n - propyl alcohol
straight chain	
CH_3- $\underset{\displaystyle CH_3}{\overset{\displaystyle \vert}{CH}}$ - CH_3 isobutane Branched chain	

Cyclic compounds : These are compounds in which molecules are formed by joining atoms to form ring like structures.

The compounds in which the ring is made of only carbon atoms are known as **homocyclic** or **carbocyclic** compounds. Carbon is an essential atom in any organic molecule. One or more hydrogen atoms are present in most of the organic molecules. All the other atoms that are found in organic molecules are called **heteroatoms**. The cyclic compounds in which the ring includes one or more heteroatoms (oxygen, nitrogen, sulphur etc.) are known as **heterocyclic** compounds.

Try this



Cyclohexene (a) Piperidine (b) Cyclopentane (c)

Benzene (d) Pyrrole (e)

i. Observe the compounds (a) to (e)
ii. Identify the compounds those contain a ring of carbon atoms only.
iii. Identify the compounds in which ring contains at least one atom other than carbon.

Alicyclic compounds : These are cyclic compounds exhibiting properties similar to those of aliphatic compounds. For example : Cyclobutane, cyclohexene. See Fig. 14.7.

Aromatic compounds : Aromatic compounds have special stability. Aromatic compounds containing benzene ring are known as benzenoid aromatics while those not containing benzene ring are called non-benzenoid aromatics. For example : benzene, tropone. See Fig. 14.7

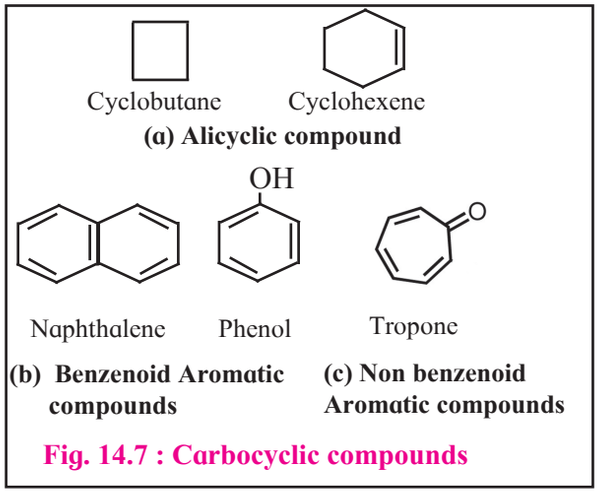


Fig. 14.7 : Carbocyclic compounds

Figure 14.8 illustrates some heterocyclic compounds

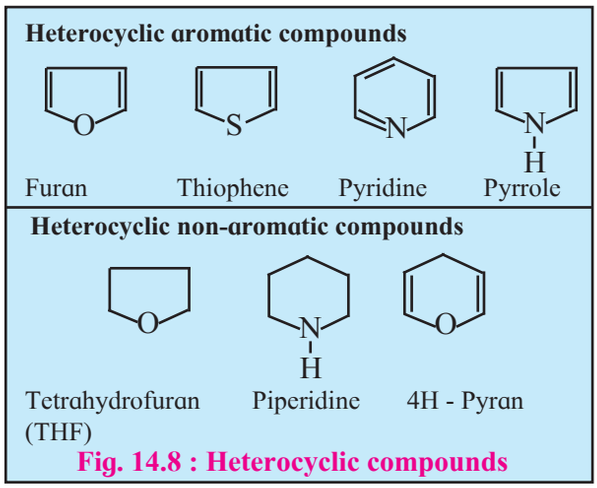


Fig. 14.8 : Heterocyclic compounds

14.3.2 Classification based on functional group :

A part of an organic molecule which undergoes change as a result of a reaction is called functional group. In the above illustration, OH is the functional group present in propanol. Inspection of structures of various organic compounds tells us that there are a large variety of functional groups present in them. The second method of classification of organic compounds is based on the nature of functional group present. The resulting individual class is called a **family** named after the constituent functional group. For example: family of alcohols, family of halogen derivatives. Table 14.3 shows some common functional groups with their names, bond structures and examples.

Homologous series : A family of functional group, in turn, comprises different homologous series. A series of compounds of the same family in which each member has the same type of carbon skeleton and functional group, and differs from the next member by a constant difference of one methylene group ($-CH_2-$) in its molecular and structural formula is called as homologous series. An individual member of a homologous series is called **homologue**. All the members, or homologues of such series are represented by the same general formula.

The members of a particular homologous series possess similar chemical properties those very gradually in their physical properties namely, melting point, boiling point, density, solubility, etc. Table 14.4 illustrates this with the help of homologous series of straight chain aldehydes having general formula $C_nH_{2n}O$.

Can you tell?

Consider the following reaction :

$$2CH_3 - CH_2 - CH_2 - OH + 2Na \longrightarrow 2CH_3 - CH_2 - CH_2 - ONa + H_2$$

Compare the structure of the substrate propanol with that of the product sodium propoxide. Which part of the substrate, the carbon skeleton or the OH group has undergone a change during the reaction ?

Do you know ?

- **Aliphatic compounds** are named so because of their attraction towards fats.
- **Aromatic compounds** are named so because some of these compounds discovered in early 19th century possessed aroma.

Table 14.3 : Functional groups in organic compounds

Sr. No.	Name of the family/ functional group	structure of the functional group	Example
1.	Halide	– X	CH_3Br methyl bromide
2.	Cyanide (or Nitrile)	– C≡ N	CH_3CN methyl cyanide (or acetonitrile)
3.	Isocyanide	$-N^{\oplus}\equiv C^{\ominus}$	CH_3NC methyl isocyanide
4.	Nitro compound/group	$-N(=O)-O^{\ominus}$ (N$^{\oplus}$)	CH_3NO_2 Nitromethane
5.	Alcohol	– OH	CH_3OH methyl alcohol
6.	Phenol	Ar – OH	C_6H_5OH Phenol
7.	Primary amine	$-NH_2$	CH_3NH_2 methyl amine
8.	Secondary amine	– NH –	$CH_3 - NH - CH_3$ Dimethyl amine
9.	Tertiary amine	$-\underset{|}{N}-$	$(CH_3)_3N$ Trimethyl amine
10.	Ether	$-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$	$CH_3 - O - CH_3$ Dimethyl ether
11.	Aldehyde	$-C(=O)-H$	CH_3CHO Acetaldehyde
12.	Ketone	$-C(=O)-$	$CH_3 - CO - CH_3$ Acetone
13.	Carboxylic acid	$-C(=O)-OH$	$CH_3 - COOH$ Acetic acid
14.	Ester	$-C(=O)-O-$	$CH_3 - COOC_2H_5$ Ethyl acetate
15.	Amide	$-C(=O)-NH_2$	$CH_3 - CONH_2$ Acetamide
16.	Secondary amide	$-C(=O)-NH-$	$CH_3 - CO - NH - CH_3$ N-methyl acetamide
17.	Tertiary amide	$-C(=O)-N<$	$CH_3 - CO - N(CH_3)_2$ N, N - dimethyl acetamide
18.	Acid anhydride	$-C(=O)-O-C(=O)-$	$CH_3 - CO - O - CO - CH_3$ Acetic anhydride
19.	Acyl chloride	$-C(=O)-Cl$	$CH_3 - COCl$ Acetyl chloride
20.	Sulphonic acid	$-S(=O)_2-O-H$	$C_6H_5SO_3H$ Benzene sulphonic acid
21.	Alkene/olefin	$>C=C<$	$CH_2 = CH_2$ Ethylene
22.	Alkyne	– C ≡ C –	CH ≡ CH Acetylene
23.	Alkane	No functional group	CH_3 - CH_3 Ethane

Problem 14.1 : Alkanes constitute a homologous series of straight chain saturated hydrocarbons. Write down the structural formulae of the first five homologues of this series. Write their molecular formulae and deduce the general formula of such homologous series.

Solution :

The first five homologues are generated by adding one - CH_2 - at a time, starting with the first homologue CH_4.

$CH_4 \xrightarrow{\text{add - } CH_2 -} CH_3 - CH_3 \xrightarrow{\text{add - } CH_2 -}$

1st homologue 2nd homologue

$CH_3 - CH_2 - CH_3$

3rd homologue

$\xrightarrow{\text{add - } CH_2 -} CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{\text{add - } CH_2 -}$

4th homologue

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

5th homologue

By counting carbon and hydrogen atoms in the five homologues we get their molecular formulae as CH_4, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}. Comparing these molecular formulae, the following general formula is deduced : $C_n H_{2n+2}$.

Problem 14.2 : Write down structural formulae of (a) the third higher and (b) the second lower homologue of CH_3CH_2COOH.

Solution :

a. structural formula of the third higher homologue is obtained by adding three – CH_2 – units to the carbon chain of given structure.

$CH_3 - CH_2 - COOH \xrightarrow[-\ CH_2 - \text{ units}]{\text{add three}}$

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - COOH$

third higher homologoue

b. structural formula of the second lower homologue is obtained by removing two – CH_2 – units from the carbon chain of the given structure.

$CH_3 - CH_2 - COOH \xrightarrow[-\ CH_2 - \text{ units}]{\text{remove two}} H - COOH$

Remember

The saturated (sp^3) carbons in a molecule are labelled as primary, secondary, tertiary and quaternary in accordance with the number of other carbons bonded to it by single bonds.

- **Primary carbon** (1^0) is bonded to only one other carbon. For example: both the carbons in ethane CH_3-CH_3.
- **Secondary carbon** (2^0) is bonded to two other carbons. For example: the middle carbon in propane CH_3-CH_2-CH_3
- **Tertiary Carbon** (3^0) is bonded to three other carbons. For example: the middle carbon in isobutane $CH_3CH(CH_3)_2$.
- **Quaternary Carbon** (4^0) in bonded to four other carbons. For example: the middle carbon in neo-pentane $C(CH_3)_4$

14.4 Nomenclature of organic compounds

14.4.1 Common/trivial names

As organic chemistry developed, attempts were made to devise a name for every organic compound. These old names are now reffered to as common / trivial names. Common name of a compound usually has some history behind and usually accepted on account of its long usage. Though a systematic method of nomenclature was developed later, common names are still useful and in many cases can not be avoided, particularly for commonly used commercial organic compounds. Stem names of certain common organic compounds are given in Table 14.5.

Table 14.4 : Homologous series of straight chain aldehydes

Name	Number of carbons	Molecular formula $C_nH_{2n}O$	Condensed structural formula	Boiling point
Formaldehyde	n = 1	CH_2O	$H-\overset{\overset{O}{\|\|}}{C}-H$	- 21^{0}C
Acetaldehyde	n = 2	C_2H_4O	$CH_3-\overset{\overset{O}{\|\|}}{C}-H$	21^{0}C
Propionaldehyde	n = 3	C_3H_6O	$CH_3-CH_2-\overset{\overset{O}{\|\|}}{C}-H$	48 ^{0}C
Butyraldehyde	n = 4	C_4H_8O	$CH_3-(CH_2)_2-\overset{\overset{O}{\|\|}}{C}-H$	75^{0}C
Valeraldehyde	n = 5	$C_5H_{10}O$	$CH_3-(CH_2)_3-\overset{\overset{O}{\|\|}}{C}-H$	103^{0}C

Table 14.5 : Trivial names of some organic compounds

Structural formula	Common Name/ Trivial Name
$CH_3 - CH_2 - CH_2 - CH_3$	n - Butane
$CH_3 - \underset{\underset{CH_3}{\|}}{CH} - CH_3$	Isobutane
$C_6H_5NH_2$	Aniline
$CH_3 - \underset{\underset{OH}{\|}}{CH} - COOH$	Lactic acid
$CHCl_3$	Chloroform
$CH \equiv CH$	Acetylene
$C_2H_5 - O - C_2H_5$	Diethyl ether
CH_3COOH	Acetic acid
$H - \underset{\underset{O}{\|\|}}{C} - H$	Formaldehyde
$CH_3 - \underset{\underset{NH_2}{\|}}{CH} - COOH$	Glycine
$\underset{\underset{OH}{\|}}{CH_2} - \underset{\underset{OH}{\|}}{CH} - \underset{\underset{OH}{\|}}{CH_2}$	Glycerol

14.4.2 IUPAC Nomenclature : With the rapidly growing number of organic compounds with increasingly complicated structures it becomes difficult to name them. Some confusion can be created when the same compound is named differently. In due course of time **International Union of Pure and Applied Chemistry (IUPAC)** was founded (1919) and a systematic method of nomenclature for organic compounds was developed under its banner. This system of nomenclature is accepted and widely used all over the world today. This system gives the unique name to each organic compound.

To arrive at the IUPAC name of an organic compound, its structure is considered to be made of three main parts : parent hydrocarbon, branches and functional groups. The IUPAC names of a compound are obtained by modifying the name of its parent hydrocarbon further incorporating names of the branches and functional groups as prefix and suffix. For doing this, certain rules were formulated by IUPAC. We consider the IUPAC rules for naming saturated and unsaturated hydrocarbons, simple monocyclic hydrocarbons, simple mono and polyfunctional compounds and substituted benzenes in the following.

14.4.3 IUPAC names of straight chain alkanes : The homologous series of straight chain alkanes forms the parent hydrocarbon part of the IUPAC names of aliphatic compounds. The IUPAC name of a straight chain alkane is derived from the number of carbon atoms it contains. Table 14.6 gives the list of the IUPAC names of first twenty straight chain alkanes. It may be noted that the stem names of first four members are accepted as their IUPAC names.

Table 14.6 : IUPAC names of the first twenty alkanes

Number of carbons	Molecular formula	Condensed formula	IUPAC name
1	CH_4	CH_4	Methane
2	C_2H_6	$CH_3 - CH_3$	Ethane
3	C_3H_8	$CH_3 - CH_2 - CH_3$	Propane
4	C_4H_{10}	$CH_3 - (CH_2)_2 - CH_3$	Butane
5	C_5H_{12}	$CH_3 - (CH_2)_3 - CH_3$	Pentane
6	C_6H_{14}	$CH_3 - (CH_2)_4 - CH_3$	Hexane
7	C_7H_{16}	$CH_3 - (CH_2)_5 - CH_3$	Heptane
8	C_8H_{18}	$CH_3 - (CH_2)_6 - CH_3$	Octane
9	C_9H_{20}	$CH_3 - (CH_2)_7 - CH_3$	Nonane
10	$C_{10}H_{22}$	$CH_3 - (CH_2)_8 - CH_3$	Decane
11	$C_{11}H_{24}$	$CH_3 - (CH_2)_9 - CH_3$	Undecane
12	$C_{12}H_{26}$	$CH_3 - (CH_2)_{10} - CH_3$	Dodecane
13	$C_{13}H_{28}$	$CH_3 - (CH_2)_{11} - CH_3$	Tridecane
14	$C_{14}H_{30}$	$CH_3 - (CH_2)_{12} - CH_3$	Tetradecane
15	$C_{15}H_{32}$	$CH_3 - (CH_2)_{13} - CH_3$	Pentadecane
16	$C_{16}H_{34}$	$CH_3 - (CH_2)_{14} - CH_3$	Hexadecane
17	$C_{17}H_{36}$	$CH_3 - (CH_2)_{15} - CH_3$	Heptadecane
18	$C_{18}H_{38}$	$CH_3 - (CH_2)_{16} - CH_3$	Octadecane
19	$C_{19}H_{40}$	$CH_3 - (CH_2)_{17} - CH_3$	Nonadecane
20	$C_{20}H_{42}$	$CH_3 - (CH_2)_{18} - CH_3$	Icosane

14.4.4 IUPAC names of branched saturated hydrocarbons

The branches or the side chains in saturated hydrocarbons are alkyl groups or alkyl substituents. Before looking at the IUPAC nomenclature of the branched saturated hydrocarbons, we look at the naming of alkyl groups.

Alkyl groups : An alkyl group may be a straight or branched chain. **A straight chain alkyl group** is generated by removing one hydrogen atom from the terminal carbon of an alkane molecule and is named by replacing 'ane' of the alkane by 'yl'. Some straight chain alkyl groups are listed in Table 14.7.

Table 14.7 : Straight chain alkyl groups

Alkane		Alkyl group		
Molecular formula	IUPAC name	Condensed formula	IUPAC name	Abbridged name
CH_4	methane	$- CH_3$	methyl	Me
C_2H_6	ethane	$- CH_2 - CH_3$	ethyl	Et
C_3H_8	propane	$- (CH_2)_2 - CH_3$	propyl	Pr
C_4H_{10}	butane	$- (CH_2)_3 - CH_3$	butyl	Bu
$C_{10}H_{22}$	decane	$- (CH_2)_9 - CH_3$	decyl	-

A branched chain alkyl group is obtained by removing a hydrogen atom from any one of the nonterminal carbons of an alkane or any hydrogen atom from a branched alkane. Stem names of branched alkyl groups containing upto four carbons are used in IUPAC names (see Table 14.8)

Table 14.8 : Trivial names of small branched alkyl groups

Structural formula	Name
$CH_3 - CH(-) - CH_3$	Isopropyl
$CH_3 - CH(CH_3) - CH_2-$	Isobutyl
$CH_3 - CH(-) - CH_2 - CH_3$	sec-Butyl
$CH_3 - C(CH_3)(CH_3) -$	tert-Butyl

Do you know ?

The group C_6H_5- (⌬) is named as phenyl group and abbriviated as Ph.

Rules for IUPAC nomenclature of branched saturated hydrocarbons :

1. Select the longest continuous chain of carbon atoms to be called the parent chain. All other carbon atoms not included in this chain constitute side chains or branches or alkyl substitutents. For example :

i. $CH_3 - CH(CH_3) - CH_2 - CH_2 - CH_3$

Parent chain has five carbon atoms and $-CH_3$ group is the alkyl sustituent.

ii. $CH_3 - CH(CH_2 - CH_2 - CH_3) - CH_2 - CH_3$

Parent chain has six 'C' atoms and methyl group is the alkyl substituent.

If two chains of equal length are located, the one with maximum number of substituents is selected as the parent chain. For example :

i. $CH_3 - CH(CH_3) - CH(CH_2 - CH_3) - CH_2 - CH_2 - CH_3$

Parent chain hexane with two alkyl substituents (correct parent chain)

$CH_3 - CH(CH_3) - CH(CH_2 - CH_3) - CH_2 - CH_2 - CH_3$

Parent chain hexane with one alkyl substituent (incorrect chain)

2. The parent chain is numbered from one end to the other to locate the position, called locant number of the alkyl substituent. The **numbering** is done in that direction which will result in lowest possible locant numbers .

$\overset{1}{C}H_3 - \overset{2}{C}H(CH_3) - \overset{3}{C}H_2 - \overset{4}{C}H_3$

(locant number : 2 ~ proper numbering)

$\overset{4}{C}H_3 - \overset{3}{C}H(CH_3) - \overset{2}{C}H_2 - \overset{1}{C}H_3$

(locant number : 3 ~ improper numbering)

3. Names of the alkyl substituents are added as **prefix** to the name of the parent alkane. Different alkyl substituents are listed in alphabetical order with each substituent name preceded by the appropriate **locant number**. The name of the substituent is separated from the locant number by **a hyphen**.

$CH_3 - CH_2 - CH(CH_3) - CH(C_2H_5) - CH_2 - CH_2 - CH_3$

The name is 4 - ethyl-3-methylheptane and not 3-methyl-4-ethylheptane.

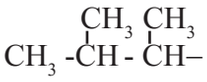
4. When both the numberings give the same set of locants, that numbering is chosen which gives **smaller locant** to the substituent having **alphabetical priority**. Thus the IUPAC name of the following structure is 3-ethyl-4-methylhexane and **not** 3-methyl-4-ethylhexane.

$CH_3 - CH_2 - CH(CH_3) - CH(CH_2 - CH_3) - CH_2 - CH_3$

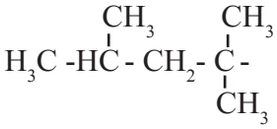
5. If two or more identical substituents are present the prefix **di** (for 2), **tri** (for 3), tetra (for 4) and so on, are used before the name of the substituent to indicate how many identical substituents are there. The locants of identical substituents are listed together, separated by **commas**.

There must be as many numbers in the name as the substituents. A digit and an alphabet is separated by hyphen. The prefixes di, tri, tetra, sec and tert are ignored in alphabetizing the substituent names. Substituent and parent hydrocarbon names are joined into **one word** (note that isopropyl comes before methyl).

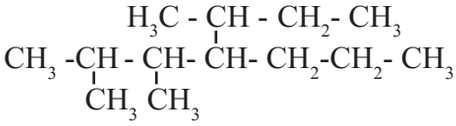
6. Branched alkyl group having no accepted trivial name is named with the longest continuous chain begining at the point of attachment as the base name. Carbon atom of this group attached to parent chain is numbered 1. Name of such substituent is enclosed in bracket. For example :



1, 2 di-methylpropyl



1, 1, 3- trimethylbutyl

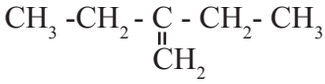


2, 3 - dimethyl - 4 - (1methylpropyl)heptane

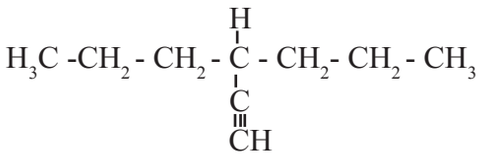
14.4.5 IUPAC nomenclature of unsaturated hydrocarbons (Alkenes and Alkynes)

While writing IUPAC names of alkenes and alkynes following rules are to be followed in addition to rules already discussed.

1. The longest continuous **chain must include** carbon-carbon **multiple bond**. Thus the longest continuous chains in I and II contain four and six carbons, respectively.



(I)



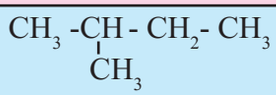
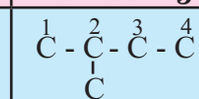
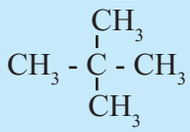
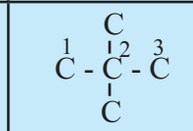
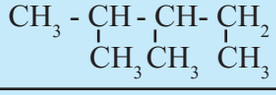
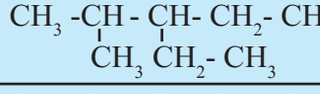
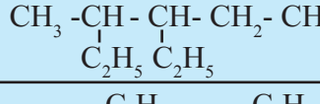
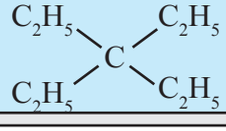
(II)

2. Numbering of this chain must be done such that carbon-carbon **multiple bond** has the **lowest possible locant** number.

Proper numbering	improper numbering
	
	

Problem 14.3 :

Complete the following table

Structural formula	Numbering	Prefix	IUPAC Name
		2 - methyl	2 - methylbutane
		2, 2 - dimethyl	2, 2-dimethylpropane
			
			
			
			

3. The ending 'ane' of alkane is replaced by 'ene' for an alkene and '**yne**' for an alkyne.

4. Position of carbon atom from which **multiple bond** starts is indicated by smaller locant number of two multiply bonded carbons before the ending 'ene' or 'yne' For example :

$CH_3 - CH_2 - CH = CH_2$	$HC \equiv C - CH_2 - CH_3$
but-1-ene	but-1-yne

5. If the multiple bond is equidistant from both the ends of a selected chain then carbon atoms are numbered from that end which is nearer to **first branching**. For example :

$$\overset{1}{CH_3}\text{-}\overset{2}{CH}(\overset{}{CH_3})\text{-}\overset{3}{CH}=\overset{4}{C}(\overset{}{CH_3})\text{-}\overset{5}{CH_2}\text{-}\overset{6}{CH_3}$$

$$\overset{1}{CH_3}\text{-}\overset{2}{CH}(\overset{}{CH_3})\text{-}\overset{3}{C}\equiv\overset{4}{C}\text{-}\overset{5}{CH_2}\text{-}\overset{6}{CH_3}$$

6. If the parent chain contains two double bonds or two triple bonds, then it is named as **diene** or **diyne**. In all these cases 'a' of 'ane' (alkane) is retained .

$$CH_3 - CH = CH - CH = CH_2$$
penta-1, 3-diene

$$CH_3 - C \equiv C - CH_2 - C \equiv C - H$$
hexa - 1, 4 -diyne

7. If the parent chain contains both double and triple bond, then carbon atoms are numbered from that end where multiple bond is nearer. Such systems are named by putting '**en**' ending first followed by '**yne**'. The number indicating the location of multiple bond is placed before the name.

$$CH_2 = CH - C \equiv C - CH_3$$
pent-1-en-3-yne

$$H - C \equiv C - CH_2 - CH = CH_2 - CH_3$$
hex-4-en-1-yne

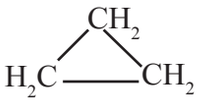
8. If there is **a tie** between a double bond and a triple bond, the double bond gets the lower number.

$H - C \equiv C - CH_2 - CH = CH_2$

pent-1-en-4-yne

14.4.6 IUPAC Names of simple monocyclic hydrocarbons : A saturated monocyclic hydrocarbon is named by attaching prefix '**cyclo**' to the name of the corresponding open chain alkane.

For example :



Cyclopropane

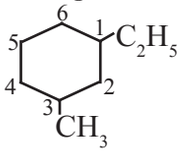
Cyclopentane

An unsaturated monocyclic hydrocarbon is named by substituting '**ene**', '**yne**' etc. for 'ane' in the name of corresponding cycloalkane. For example:

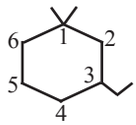
Cyclohexene

Cyclopentene

If side chains are present then the above discussed rules are applied. **Numbering** of the ring carbon is **started from a side chain**. For example :



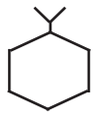
1 - ethyl - 3 - methylcyclohexane



3 - ethyl - 1, 1 - dimethylcyclohexane

If alkyl groups contain greater number of carbon atoms than the ring, the compound is named as derivative of alkane. Ring is treated as substituent. For example :

3 - cyclopropylhexane



isopropylcyclohexane

14.4.7 IUPAC nomenclature of compounds containing one or more functional groups :

The IUPAC names of compounds containing one or more functional groups include the names of the functional groups as prefix and/ or suffix. Table 14.8 shows how names of functional groups are modified when included as prefix or suffix in the IUPAC name. Some functional groups appear only as prefixes and are shown in Table 14.9. (a and b)

Table 14.9 : Modified names of functional groups as in IUPAC nomenclature

a. Functional groups appearing prefix and suffix

Functional group	Prefix	Suffix
– COOH	carboxy	– oic acid
– COOR	alkoxycarbonyl	– oate
– COCl	chlorocarbonyl	– oyl chloride
– $CONH_2$	carbamoyl	– amide
– CN	cyano	– nitrile
– CHO	formyl	– al
– CO –	oxo	– one
– OH	hydroxy	– ol
– NH_2	amino	– amine

b. Functional groups appearing only as prefix

Functional group	Prefix
– NO_2	nitro
– X (– F, – Cl, – Br, – I.)	halo (fluro, chloro, bromo, iodo)
– OR (– OCH_3, – OC_2H_5, etc)	alkoxy (methoxy, ethoxy, etc.)

Naming monofunctional compounds : When a molecule contains only one functional group, the longest carbon chain containing that functional group is identified as the parent chain and numbered so as to give the smallest locant number to the carbon bearing the functional group. The parent name is modified by applying appropriate suffix. Location of the functional group is indicated where necessary and when it is NOT '1'.

For example :

$CH_3 - CH_2 - CH_2 - COOH$

butanoic acid (No need to mention -1-)

$CH_3 - CH_2 - C \equiv N$

propanenitrile (No need to mention -1-)

$CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - CH_3$

pentan-2-one (Necessary to mention -2-)

$CH_3 - \overset{\overset{O}{\|}}{C} - CH_2 - CH_3$

butanone (No need to mention -2-)

When the functional group cannot be used as suffix, and can be only the prefix, the molecule is named as parent alkane carrying the functional group as substituent at specified carbon. For example :

$H_3C - CH_2 - CH_2 - NO_2$

1 - Nitropropane

$CH_3 - \underset{\underset{OCH_3}{|}}{CH} - CH_3$

2- Methoxypropane

Polyfunctional compounds : The organic compounds possessing two or more functional groups (same or different) in their molecules are called polyfunctional compounds. When there are two or more different functional groups, one of them is selected as the **principal functional group** and the others are considered as substituents. The principal functional group is used as suffix of the IUPAC name while the other substituents are written with appropriate perfixes. The principal functional group is decided on the basis of the following order of priority.

$- COOH > - SO_3H > - COOR > - COCl > - CONH_2 > - CN > - CHO > \diagup\!\!\diagdown C = O > - OH > - NH_2 > \underset{|}{C} = \underset{|}{C} > - C \equiv C -$

IUPAC Rules for naming mono or polyfunctional compounds

i. The longest carbon **chain containing** or bearing the single or the **principal functional group** is identified as parent chain. Ether is named as alkoxyalkane. While naming it, the larger alkyl group is chosen as parent chain.

Numbering of parent chain is done so as to give the **lowest** possible **locant** numbers to the carbon atom of this functional group.

ii. The name of the parent hydrocarbon is modified adequately with **appropriate suffix** in accordance with the single/principal **functional group**.

iii. Names of the **other functional groups** (if any) are attached to this modified name as **prefixes**. The locant numbers of all the functional groups are indicated before the corresponding suffix/prefix. The carbon atom in - COOR, - COCl, $-CONH_2$, - CN and - CHO is C - 1 by rule and therefore, is not mentioned in the IUPAC name.

Problem 14.4 : Write IUPAC names for the following structures :

i. $CH_3 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{O}{||}}{C} - CH_2 - CH_3$

ii. $CH_3 - \underset{\underset{NH_2}{|}}{CH} - CH_2 - COOH$

iii. $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_2 - OH$

iv. $CH_2 = CH - CH = CH_2$

Solution :

i. $CH_3 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{O}{||}}{C} - CH_2 - CH_3$

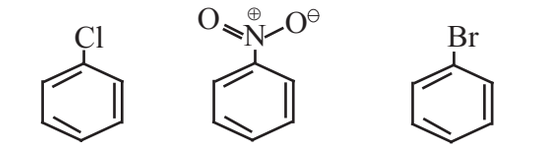
Here the principal functional group, ketone is located at the C-3 on the five carbon chain. The -OH group, the hydroxyl substituent is at C-2. Therefore the IUPAC name is 2-hydroxypentan-3-one.

ii. $CH_3 - \underset{\underset{NH_2}{|}}{CH} - CH_2 - COOH$

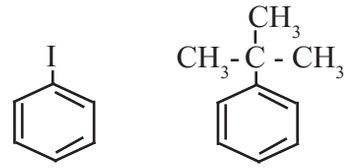
Here the principal functional group is carboxylic acid. The amino substituent is located at C-3 on four carbon chain. Therefore the IUPAC name 3-aminobutanoic acid.

14.4.8 IUPAC nomenclature of substitued benzene

I. Monosubstituted benzene : The IUPAC name of a monosubstituted benzene is obtained by placing the name of substituent as prefix to the parent skeleton which is benzene. For example :

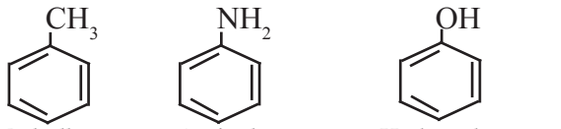


Chlorobenzene Nitrobenzene Bromobenzene

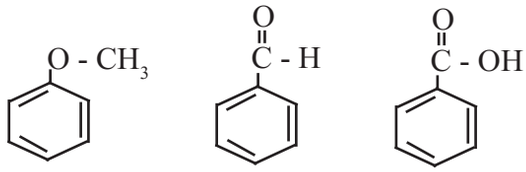


Iodobenzene tert- Butylbenzene

Some monosubstituted benzenes have trivial names which may show no resemblance with the name of the attached substituent group. For example, methylbenzene is known as **toluene**, aminobenzene as aniline, hydroxybenzene as phenol and so on. The common names written in the bracket are also used universally and accepted by IUPAC.



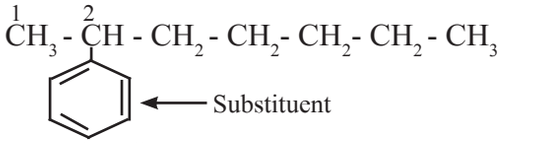
Methylbenzene (Toluene) Aminobenzene (Aniline) Hydroxybenzene (Phenol)



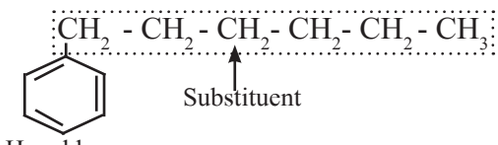
Methoxybenzene (Anisole) Benzaldehyde Benzoic acid

If the alkyl substituent is larger than benzene ring (7 or more carbon atoms) the compound is named as phenyl-substituted alkane.

For example :

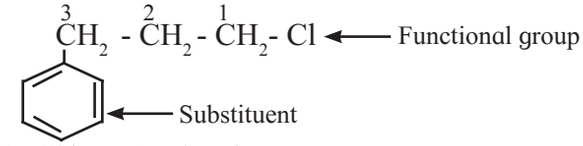


2 - Phenylheptane

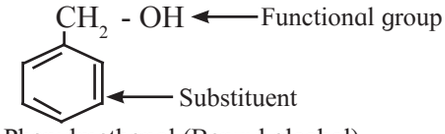


Hexyl benzene

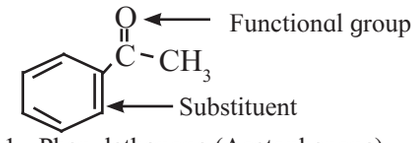
Benzene ring can as well be considered as substituent when it is attached to an alkane with a functional group.



1 - Chloro - 3 - phenylpropane



Phenylmethanol (Benzyl alcohol)

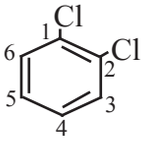


1 - Phenylethanone (Acetophenone)

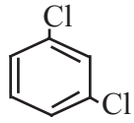
II. Disubstituted benzene derivatives :

Common names of the three possible isomers of disubstitued benzene derivatives are given using one of the prefixes ortho (o-), meta (m-) or para (p-).

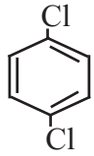
IUPAC system, however, uses numbering instead of prefixes, o-, m-, or p-.



1,2 - dichlorobenzene
(o - Dichlorobenzene)

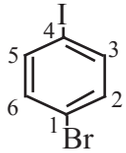


1,3 - dichlorobenzene
(m - Dichlorobenzene)

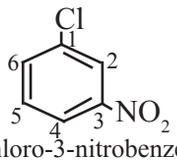


1,4 - dichlorobenzene
(p - Dichlorobenzene)

If two substituents are different, then they enter in alphabetical order.

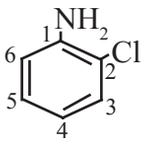


1-bromo-4-iodobenzene
(p - Bromoiodobenzene)

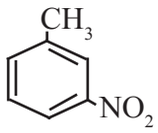


1-chloro-3-nitrobenzene
(m-Chloronitrobenzene)

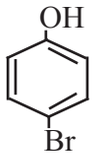
If one of the two groups gives special name to the molecule then the compound is named as derivative of that special compound.



2 - chloroaniline
(o - Chloroaniline)

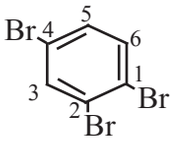


3 - nitrotoluene
(m - Nitrotoluene)

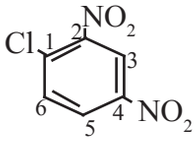


4 - Bromophenol
(p - bromophenol)

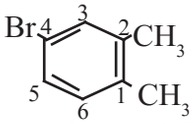
III. Trisubstituted benzene derivatives : If more than two substituents are attached to benzene ring, numbers are used to indicate their relative positions following the alphabetical order and lowest locant rule. In some cases, common name of benzene derivatives is taken as parent compound. For example :



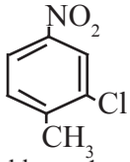
1,2,4-Tribromobenzene



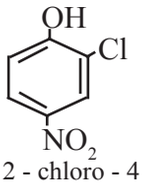
1 - chloro - 2, 4
-dinitrobenzene



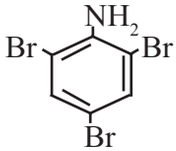
4 - bromo - 1, 2
-dimethylbenzene



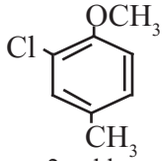
2 - chloro - 1 - methyl
- 4 - nitrobenzene



2 - chloro - 4 -
nitrophenol



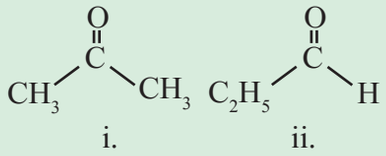
2, 4, 6 -
tribromoaniline



2 - chloro - 4 -
methylanisole

14.5 Isomerism

Activity :



i. ii.

a. Observe the structural formulae (i) and (ii)
b. Find out their molecular formulae
c. What is the difference between them ?
d. What is the relation between the two compounds represented by these structural formulae ?

The phenomenon of existence of two or more compounds possessing the same molecular formula is known as **isomerism**. Such compounds are known as isomers of each other. Two types of isomerism are observed in the organic compounds, namely, **structural isomerism** and **stereoisomerism**. When two or more compounds have the same molecular formula but different structural formulae, it is called structural isomerism. On the other hand, when different compounds have the same structural formula but different relative arrangement of groups / atoms in space, that is, different spatial arrangement of groups / atoms it is called stereoisomerism. In this chapter we are going to look at some details of only structural isomerism.

14.5.1 Structural isomerism

We have seen in the begining of this chapter that the structural formula describes the sequence in which the constituent atoms of a molecule are bonded and the nature of the bonds between them. **When two or more compounds have same molecular formula and different structural formula they are said to be structural isomers of each other. The phenomenon is known as structural isomerism**. Structural isomerism is further classified as **chain isomerism**, **position isomerism**, **functional group isomerism**, **metamerism and tautomerism**. Figure 14.9 shows various types of isomerism.

a. Chain isomerism : When two or more compounds have the same molecular formula but different parent chain or different carbon skeleton, it is refered to as chain isomerism and such isomers are known as chain isomers. For example : Butane (CH_3 - CH_2 - CH_2 - CH_3) and 2-methylpropane [CH_3 - $CH(CH)_3$ -CH_3] are chain isomers of each other as they have different carbon skeletons and the same molecular formula C_4H_{10}.

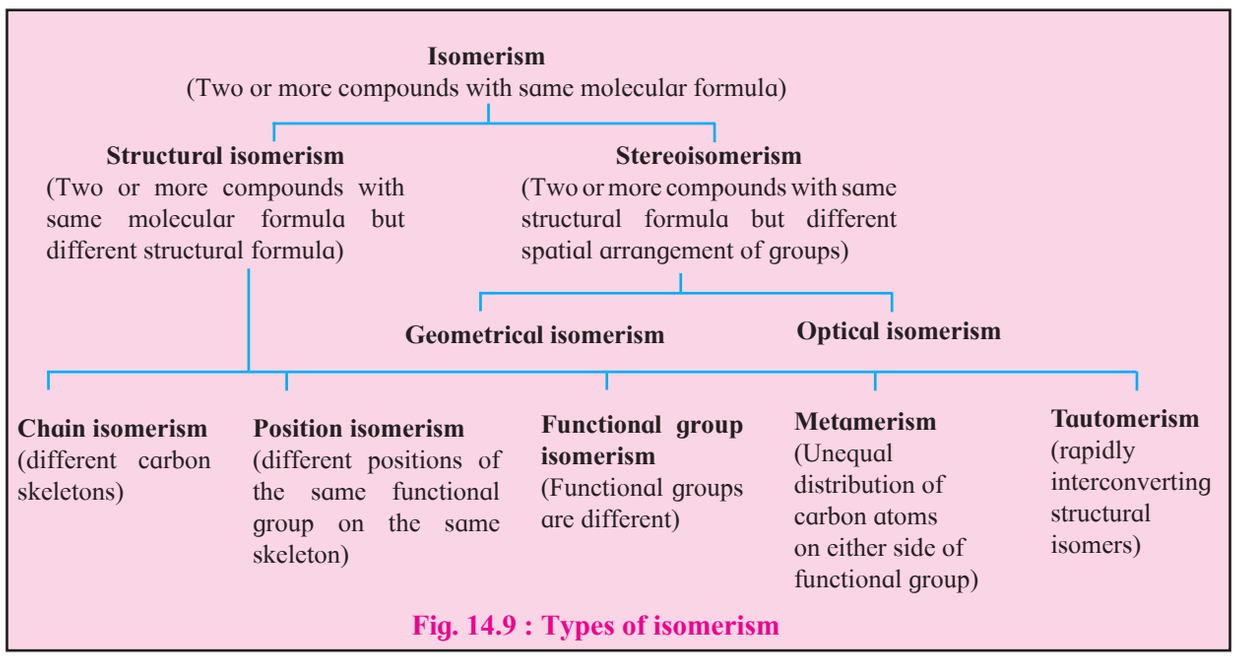


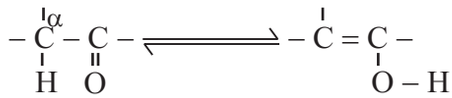
Fig. 14.9 : Types of isomerism

b. Position isomerism : The phenomenon in which different compounds having the same functional groups at different positions on the parent chain is known as position isomerism.
For example : But-2-ene [CH_3 - CH = CH - CH_3] and but-1-ene [CH_2 = CH - CH_2 - CH_3] are position isomers of each other as they have the same molecular formula C_4H_8 and the same carbon skeleton but the double bonds are located at different positions.

c. Functional group isomerism : The phenomenon in which different compounds with same molecular formula have different functional groups is known as functional group isomerism. For example : Dimethylether ($CH_3 - O - CH_3$) and ethyl alcohol ($CH_3 - CH_2 - OH$) have same molecular formula C_2H_6O but the former has ether (– O –) functional group and the latter has alcohol (– OH) functional group.

d. Metamerism : Different compounds with the same molecular formula and the same functional group, but having unequal distribution of carbon atoms on either side of the functional group is refered to as metamerism and the isomers are known as metamers. For example : Ethoxyethane ($CH_3 - CH_2 - O - CH_2 - CH_3$) and methoxypropane ($CH_3 - O - CH_2 - CH_2 - CH_3$) have the same molecular formula $C_4H_{10}O$ and the same functional group ether but have different distribution of carbon atoms attached to etheral oxygen. These are metamers of each other.

e. Tautomerism : Same compounds exists as mixture of two or more stucturally distinct molecules which are in rapid equilibrium with each other. This phenomenon is referred to as tautomerism. Such interconverting isomers are called tautomers. In nearly all the cases, it is the proton which shifts from one atom to another atom in the molecule to form its tautomer.

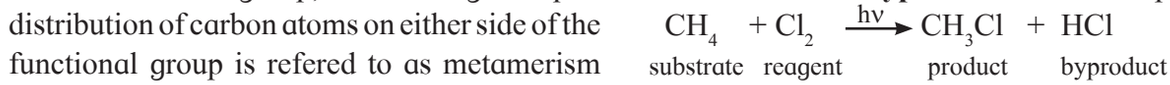


Keto form Enol form

For example : **Keto-enol tautomerism** is very common form of tautomerism. It is found in carbonyl compounds. Here a hydrogen atom shifts reversibly from the α - carbon of the keto form to oxygen atom of the enol.

14.6 Theoretical basis of organic reactions :

All the organic molecules primarily contain various types of covalent bonds between the constituents atoms. During an organic reaction, molecules of the reactant undergo change in their structure. A covalent bond at a carbon atom in the reactant is broken and a new covalent bond is formed at it, giving rise to the product. Often this change is brought about by means of another reactant. The reactant that provides carbon to the new bond is called **substrate.** The other reactant which brings about this change is called **reagent**. In case both the reactants provide carbon atoms to a new bond, the reactant considered is called substrate. Apart from the product of interest some other products are formed in a reaction. These are called **byproducts**. For example :



substrate reagent product byproduct

Covalent bonds are made of valence electrons of the constituent atoms. Redistribution of valence electrons of constituent atoms results in the **bond breaking** or **bond forming** processes along the organic reaction; and which are usually not instantaneous. As a result, the overall organic reaction is punctuated by formation of one or more unstable species called **intermediates**. Overall the organic reaction is often a **multi-step process**.

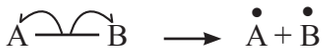
A sequential account of (i) the electron movement taking place during each step (ii) the bond cleavage and/or bond formation (iii) accompanying changes in energy and shapes of various species and (iv) rate of the overall reaction. The individual steps, constitue the **reaction mechanism**. The knowledge of mechanism of a reaction is useful for **understanding the reactivity** of the concerned organic compounds and, in turn, helpful for **planning synthetic strategies**.

In the following subsection we are going to look at the types of bond cleavage, types of reagents, the factors that influence stability of various species involved and representation of electron movement occuring during organic reactions.

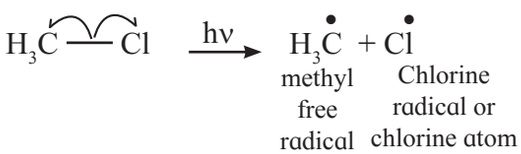
14.6.1 Types of cleavage of covalent bond

A covalent bond can undergo cleavage or fission in two ways (i) **Homolytic cleavage**, (ii) **Heterolytic cleavage**

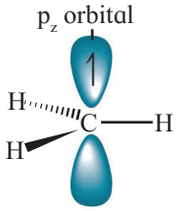
A covalent bond comprises two electrons (bond pair of electrons) shared between the two bonded atoms. In **homolytic cleavage** of a covalent bond one of the two electrons goes to one of the bonded atoms and the other is bound to the other. Movement of a single electron is represented by a half headed curved arrow or fish hook ( ). The tail of the curved arrow indicates the place from where the electron is removed while the head of the curved arrow indicates the place where the electron reaches as the result of the movement. Such homolytic cleavage of a covalent bond gives rise to two neutral species carrying one unpaired electron each. A species with single unpaired electron is called **'free radical'** or sometimes just '**radical**'. A free radical is unstable and thereby a reactive species, having a tendency to seek an electron for pairing. A homolytic cleavage, thus, is represented as :



For example,

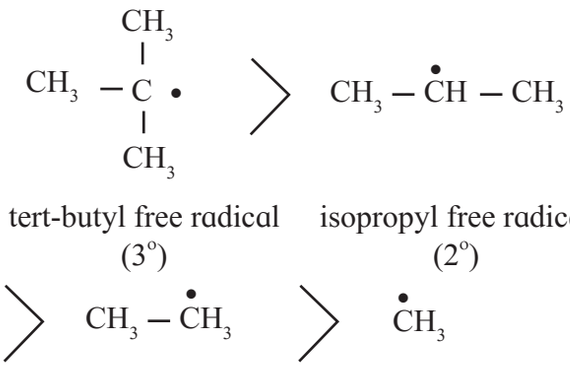


Homolytic fission is favoured in the presence of ultravoilet radiation or suitable peroxides or at high temperatures. The organic reactions which proceed by homolytic fission are known as **free radical or non-polar reactions**. Free radicals have only transitory existence. These are formed as reaction intermediate which subsequently react with another radical/molecule to restore stable bonding pair. A carbon free radical is sp^2 hybridized and reveals planar trigonal geometry.

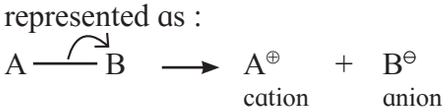


Shape of methyl free radical

Alkyl free radicals are classified as primary (1^0), secondary (2^0) and tertiary (3^0). The observed stability order of alkyl free radicals is :



In **heterolytic cleavage** of covalent bond both shared electrons go to one of the two bonded atoms. This turns out to be the more electronegative atom of the two. Movement of an electron pair is represented by a curved arrow ( ). Heterolytic cleavage of a covalent bond gives rise to two **charged species**, one with negative charge and the other with positive charge. The negatively charged (anionic) species has the more electronegative atom which has taken away the shared pair of electron with it. A heterolytic cleavage is represented as :



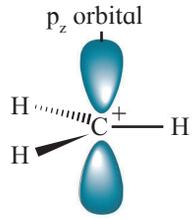
(B is more electronegative than A)

$$H_3C \overset{\curvearrowright}{-} Br \longrightarrow \underset{\text{methyl carbocation}}{H_3C^{\oplus}} + \underset{\text{bromide}}{Br^{\ominus}}$$

(Br is more electronegative than C)

Heterolysis is favoured in polar solvents. In methyl bromide, bromine is more electronegative. Thus heterolysis of methyl bromide results in formation of methyl carbocation and bromide anion.

A carbon atom having sextet of electrons and a positive charge is known as **carbocation** (earlier called carbonium ion). Carbocations are highly unstable and reactive species formed as intermediates in many organic reactions.



Shape of methyl carbocation

The central carbon atom of a carbocation is sp^2 hybrid state and has trigonal planar geometry. The p_z atomic orbital is vacant and is perpendicular to the plane containing the three sigma bonds at the carbon.

Carbocations are classified as primary (1^0), secondary (2^0) and tertiary (3^0). The observed stability of alkyl carbocations follows the order :

$$(CH_3)_3\overset{\oplus}{C} > CH_3 - \overset{\oplus}{C}H - CH_3 > CH_3 - \overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$$

t-butyl carbocation > iso-propyl carbocation > ethyl carbocation > methyl carbocation

Heterolytic bond fission generates a species called **carbanion** in which carbon gets the shared pair of electrons. This happens when a carbon atom is bonded to the electropositive atom.

$$H_3C \overset{\curvearrowleft}{-} Z \xrightarrow{\text{Heterolysis}} H_3C^{\ominus} + Z^{\oplus}$$

(Z is more electropositive than C)

The central carbon atom of a carbanion has completed octet of electrons and a negative charge. The carbanion is unstable and reactive which is formed as the reaction intermediate. Heterolytic fission is favoured in the polar solvents. The organic reactions proceed via heterolytic fission known as **heteropolar / polar / ionic reactions**. Most organic reactions taking place in solutions follow ionic mechanism.

Can you tell?

Some bond fissions are described in the following table. For each of them, show the movement of electron/s using curved arrow notation. Classify them as homolysis or heterolysis and idetify the intermediate species produced as carbacation, carbonion or free radical.

Bond fission	Types of cleavage	Intermediate
$\overset{\curvearrowleft}{CH_3} - Cu \longrightarrow CH_3^{\ominus} + Cu^{\oplus}$	heterolysis	carbanion
$C_6H_5 - \ddot{O} - \ddot{O} - C_6H_5 \longrightarrow 2C_6H_5\ddot{O}\cdot$	.....	.....
$CH_3 - \overset{O}{\overset{\|}{C}} - CH_2 - H + \overset{\ominus}{O}H \longrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - \overset{\ominus}{C}H_2 + H_2O$	.....	.....
$CH_3 - \overset{CH_3}{\underset{CH_3}{\overset{\|}{\underset{\|}{C}}}} - Br \longrightarrow \overset{CH_3}{\underset{CH_3}{\overset{\|}{\underset{\|}{C^{\oplus}}}}} + Br^{\ominus}$	.....	.....
$CH_3 - CN \longrightarrow \overset{\oplus}{C}H_3 + \overset{\ominus}{C}N$	.....	.....

14.6.2 Types of reagent

Can you recall?

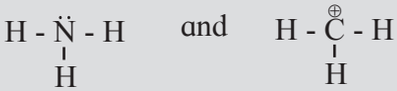
1. What is meant by 'reagent' ?
2. Identify the 'reagent', 'substrate', 'product' and 'byproduct' in the following reaction.

$CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$

The **polar organic reactions** are brought about by two types of reagents. Depending upon their ability to accept or donate electrons from or to the substrate, reagents are classified as (i) Electrophiles ($E^{\oplus}$) (ii) Nucleophiles (Nu:) **Electrophiles** (meaning electron loving spicies) accept electrons from the substrate. Thus electrophiles are electron seeking species. This is because they themselves are electron deficient. For example ; a positively charged ion such as $Br,^{\oplus}CH_3$ or a neutral species having a vacant orbitals such as $AlCl_3$. **Nucleophiles** (nucleus seeking species) give away electrons to the substrate. This is because nucleophiles are electron rich species. For example : negatively charged species such as $OH^{\ominus}$ or neutral species such as $H_2\ddot{O}$, having lone pair of electrons.

Problem 14.5 : Identify the nucleophile and electrophile from NH_3 and $CH_3^{\oplus}$. Also indicate the nucleophilic and electrophilic centres in them. Justify.

Solution : The structural formulae of two reagents showing all the valence electrons are :



Thus NH_3 contains N with a lone pair of electrons which can be given away to another species. Therefore NH_3 is a nucleophile and 'N' in it is the nucleophilic centre. The $CH_3^{\oplus}$ is a positively charged electron deficient species having a vacant orbital on the carbon. It is an electrophile. The 'C' in it is the electrophilic centre.

A polyatomic electrophile has an electron deficient atom in it called the **electrophilic centre**, while a polyatomic nucleophile has an electron rich atom in it is called the **nucleophilic centre**. For example : the electrophilic centre of the electrophile $AlCl_3$ is Al which has only 6 valence electrons. The nucleophilic centre of the nucleophile H_2O is 'O' which has two lone pairs of electrons.

A nucleophile attacks the electrophilic centre in the substrate and brings about a nucleophilic reaction. On the other hand an electrophile attacks a nucleophilic centre in the substrate and brings about an electrophilic reaction. This principle is illustrated in the following simple reaction though, it is not an organic reaction.

Here the nucleophilic centre $\ddot{N}$ in the nucleophile NH_3 attacks the electrophilic centre 'B' in the electrophile BF_3 and gives the product.

14.6.3 Electronic effects in organic reaction

We noted earlier that in polar organic reactions the nucleophilic centre in a nucleophile attacks the electrophilic centre in the substrate whereas the electrophilic centre in an electrophile attacks the nucleophilic centre in the substrate. **How electrophilic or nucleophilic centre generated in a neutral substrate ?** This happens because of displacement of valence electrons within some organic molecules, which results in their polarization. **The displacement of valence electrons resulting in polarization of an organic molecule is called electronic effect.** The electronic effect that occurs in the **ground state** is **permanent** effect. This takes place due to influence of certain atom or substituent or certain structural feature present in the molecule. **Inductive effect** and **resonance effect** are two examples of permanent electronic effect.

On the other hand the electron displacement effect occuring in a substrate due to approach of the attacking reagent is a **temporary effect**. This type of electronic effect is called **electromeric effect or polarisability effect**. We consider various types of electronic effects in the following sections.

14.6.4 Inductive effect

Can you recall?

- How is covalent bond formed between two atoms ?
- Consider two covalently bonded atoms Q and R where R is more electronegative than Q. Will these atoms share the electron pair equally between them ?
- Represent the above polar covalent bond between Q and R using fractional charges $\delta^{\oplus}$ and $\delta^{\ominus}$.

We learnt earlier that covalent bond between two atoms differing in their electronegativity is polar covalent bond. For example : the covalent bond between carbon and more electronegative chlorine is a polar covalent bond. **When an organic molecule has a polar covalent bond in its structure, polarity is induced in adjacent carbon-carbon single bonds too. This is called inductive effect.** Consider, for example, the chloroethane molecule :

$$\overset{2}{C}H_3 - \overset{1}{C}H_2 - Cl$$

In this molecule a positive polarity is developed on C^2 by inductive effect of the Cl atom bonded to C^1. Normally the C^2 - C^1 bond would not be expected to be polar as it is a covalent bond between two atoms of the same element carbon. Yet this bond aquires some polarity, because of the presence of chlorine atom in the molecule. Chlorine being more electronegative than carbon, the C^1 - Cl bond is a polar covalent bond with partial negative charge on Cl and equal amount of partial positive charge on C^1. As the C^1 is further bonded to C^2, the positive polarity of C^1 pulls the shared pair of electrons of the C^2 - C^1 bond more towards itself. As a result a part of partial positive charge produced on C^1 is transfered to C^2. This results in developing a still smaller positive charge on C^2. In other words, the electron density gets displaced towards the chlorine atom not only along the C^1 - Cl bond, but also along the C^2 - C^1 bond due to the inductive effect of Cl. This is represented as :

$$\overset{2}{C}H_3 \longrightarrow \overset{1}{C}H_2 \longrightarrow Cl$$

The **arrow head** put **in the centre of the bond** is used to **represent the inductive effect**. The direction of the arrow head indicates the direction of the permanent electron displacement taken place along the sigma bond in the ground state.

Inductive effect of an influencing group is transfered to subsequent carbon atoms along the chain of C - C bonds, as it decreases rapidly as the number of intervening C - C bonds increases and becomes negligibly small beyond three bonds. This can be represented as

$$CH_3 - \overset{\delta_3\oplus}{C}H_2 \longrightarrow \overset{\delta_2\oplus}{C}H_2 \longrightarrow \overset{\delta_1\oplus}{C}H_2 \longrightarrow \overset{\delta\ominus}{Cl}$$

Where $\delta_3\oplus < \delta_2\oplus < \delta_1\oplus$

The direction of the inductive effect of a bonded group depends upon whether electron density of the bond is withdrawn from the bonded carbon or donated by the bonded carbon. According to this ability the groups substituents are classified as either **electron withdrawing** (accepting) or **electron donating** (releasing) groups with respect to hydrogen.

In the above example, electron displacement takes place towards chlorine. This means that Cl withdraws electron density from the carbon chain and is electron withdrawing. Chlorine is said to exert an **electron withdrawing inductive effect or negative inductive effect (-I effect)** on the carbon chain. Some other groups having - I effect are - NO_2 (nitro), - CN (cyano), - COOH (carboxy), - COOR (ester), - OAr (aryloxy).

On the other hand alkyl groups (-CH_3, -CH_2-CH_3) are considered as groups exerting **electron releasing inductive effect (+I effect) on the carbon chain**.

Problem 14.6 : Consider the following molecules and answer the questions,
CH_3- CH_2- CH_2- Cl, CH_3- CH_2- CH_2- Br, CH_3- CH_2- CH_2- I.
(i) What type of inductive effect is expected to operate in these molecules ?
(ii) Identify the molecules from these three, having the strongest and the weakest inductive effect.
Solution : (i) The groups responsible for inductive effect in these molecules are -Cl, -Br and -I, respectively. All these are halogen atoms which are more electronegative than carbon and therefore all of them exert - I effect, that is, electron withdrawing inductive effect.
(ii) The - I effect of halogens is due to their electronegativity. A decreasing order of electronegativity in these halogens follows Cl > Br > I. Therefore the strongest -I effect is expected in CH_3 - CH_2 - CH_2 - Cl, while the weakest -I effect is expected for CH_3- CH_2- CH_2- I.

Problem 14.7 : Which of the CH_3 - $CHCl_2$ and CH_3CH_2Cl is expected to have stronger -I effect ?
Solution : The group exerting -I effect in CH_3CH_2Cl is one - Cl while in CH_3 - $CHCl_2$ there are two - Cl atoms. Therefore CH_3 - $CHCl_2$ is expected to have strong -I effect.

14.6.5 Resonance structures

Try this

1. Draw a bond line structure of benzene (C_6H_6)
2. How many C - C and C = C bonds are there in this structure ?
3. Write down the expected values of the bond lengths of the carbon carbon bonds in benzene (refer to Table 5.7).

The cyclic structure of benzene incorporating three alternating C-C single bonds and C=C double bonds implies two distinct bond length of 154 pm and 133 pm respectively (refer to Table 5.2 and see Fig. 14.10). Experimental measurements show that benezene has a regular hexagonal shape and all the six carbon bonds, have the same bond length of 138 pm which is intermediate between C-C single bond and C=C double bond. This means that all the six carbon carbon bonds in benzene are equivalent, unlike what appears from the single Lewis structure.

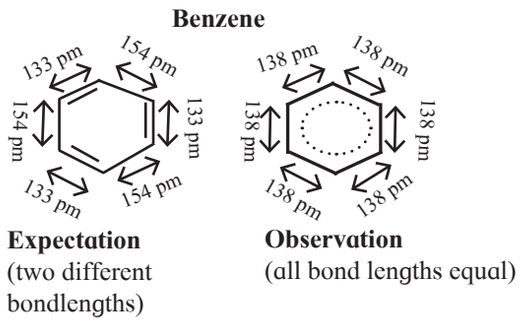


Fig 14.10 Structure of Benzene

Can you recall?

- Write down two Lewis structures for ozone. (Refer to chapter 5)
- How are these two Lewis structures related to each other ?
- What are these two Lewis strucutres called ?

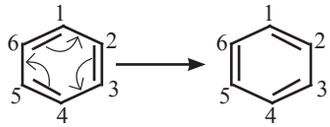
When Lewis structure of a compound has two or more multiple bonds alternating with single bonds, it is called **a conjugated system of π bonds**. In such a system or in species having an atom carrying p orbital attached to a multiple bond, **resonance theory** is applicable.

We understand the following points from the resonance theory :

(i) The π electrons in conjugated system of π bonds are not localized to a particular π bond.

(ii) For a compound having a conjugated system of π bonds (or similar other systems) two or more Lewis structures are written by showing movement of π electrons (that is delocalization of π electrons) using curved arrows.

The Lewis structures so generated are linked by **double headed arrow** and are called **resonance strucutres** or **contributing structures** or **cononical structures** of the species. Thus, two resonance structures can be drawn for benzene by delocalizing or shifting the π electrons :



I II

(iii) The positions of the carbon atoms in the conjugated system of π bonds remain unchanged, but the positions of π electrons are different in different resonance structures. For example, in the resonance structure I of benzene there is a single bond between C^1 and C^2 while in the resonance structure II there is a double bond between C^1 and C^2.

(iv) Any resonance structure is hypothetical and does not by itself represent any real molecule and can explain all the properties of the compound. The real molecule has, however, character of all the resonance structures those can be written. The real or actual molecule is said to be the **resonance hybrid** of all the resonance structures. For example an actual benezene molecule is the resonance hybrid of structures I and II and exhibit character of both these structures. Its approximate representation can be shown as a dotted circle inscribed in a regular hexagon. Thus each carbon carbon bond in benzene has single as well as double bond character and the ring has a regular hexagonal shape.

Resonance hybrid of structures I and II

(v) Hypothetical energy of an individual resonance structure can be calculated using bond energy values. The energy of actual molecule is, however, lower than that of any one of the resonance structures. In other words, **resonance hybrid is more stable** than any of the resonance structures. The difference in the actual energy and the lowest calculated energy of a resonance structure is called **resonance stabilization energy** or just **resonance energy**. Thus, resonance leads to stabilization of the actual molecule.

Problem 14.8 : Identify the species that contains a conjugated system of π bonds. Explain your answer.

$CH_2 = CH - CH_2 - CH = CH_2$

I

$CH_2 = CH - CH = CH - CH_3$

II

Solution : I Does not contain conjugated system of π bonds, as the two C = C double bonds are separated by two C - C single bonds.

II Contains a conjugated system of π bonds, as the two C = C double bonds are saparated by only one C - C single bond.

Rules to be followed for writing resonance structure :

(i) Resonance structures can be written only when all the atoms involved in the π conjugated system lie in the same place.

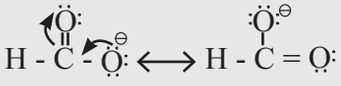
(ii) All the resonance structures must have the same number of unpaired electrons.

(iii) Resonance structures contribute to the resonance hybrid in accordance to their energy or stability. More stable (having low energy) resonance structures contribute to largely and thus are important.

Thus, between the compared resonance structures, that resonance structure is more stable and therefore important which has (a) more number of covalent bonds, (b) more number of atoms with complete octet or duplet, (c) less separation, if any, of opposite charges, (d) negative charge, if any, on more electronegative atom and positive charge, if any, on more electropositive atom and (e) more dispersal of charge.

Problem 14.9 : Write resonance structures of H - $COO^{\ominus}$ and comment on their relative stability.

Solution : First the detailed bond structure of H - $COO^{\ominus}$ showing all the valence electron is drawn and then other resonance strucutres are generated using curved arrow to show movement of π-electrons. Two resonance structures are written for H - $COO^{\ominus}$.



I II

Both the resonance structures I and II are equivalent to each other, and therefore, are equally stable.

Problem 14.10 : Identify the species which has resonance stabilization. Justify your answer.

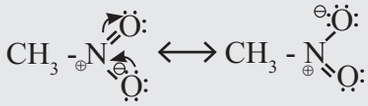
(i) $CH_3 - \ddot{O} - H$ (ii) $CH_3 - NO_2$

(iii) buta - 1, 3 - diene

Solution :

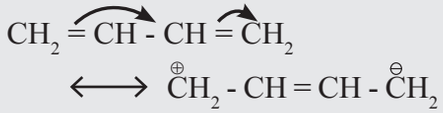
(i) The bond structure shows that there is no π bond. Therefore no resonance and no resonance stabilization.

(ii)



N= O double bond is attached to 'O' which carries lone pair of electrons in a p orbital. Therefore resonance strucutres can be written and species is resonance stabilized.

(iii)

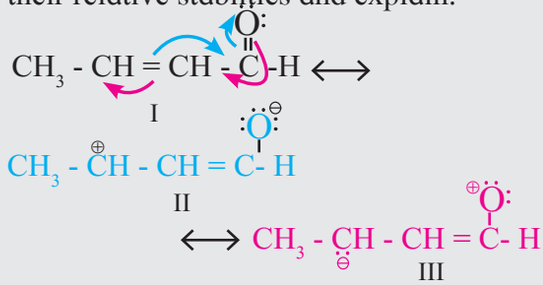


The Lewis structure shows two C=C double bonds alternating with a C-C single bond. Therefore resonance structures can be written as shown, and the species is resonance stabilized.

Remember

When all the resonance structures of a species are equivalent to each other, the species is highly resonance stabilized. For example, R - $COO^{\ominus}$, $CO_3^{2\ominus}$

Problem 14.11 : Write three resonance structures for CH_3-CH = CH-CHO. Indicate their relative stabilties and explain.



Stabilty order : I > II > III

I : Contains more number of covalent bonds, each carbon atom and oxygen atom has complete octet, and involves no separation of opposite charges. Therefore the most stable resonance structure.

II : Contains one covalent bond less than in I, one carbon ($C^{\oplus}$) has only 6 valence electrons, involves separation of opposite charges; the resonance structure II has -ve charge on more electronegative 'O' and +ve charge on more electroposoitve 'C'. It has intermediate stability.

III : Contains one covalent bond less than in I, oxygen has only 6 valence electrons, involves separation of opposite charge , has -ve charge on the more electropositive 'C' and +ve charge on more electronegative 'O'. All these factors are unfavourable for stability. Therefore it is the least stable.

14.6.6 Resonance Effect : The existence of resonance often results in developing polarity in a molecule**. The polarity produced in the molecule by the interaction between conjugated π bonds (or that between π bond and p orbital on attached atom) is called the resonance effect** or **mesomeric effect**. The effect is transmitted through a chain of conjugated π bonds. There are two types of resonance effects (or mesomeric effect) designated as positive resonance effect (+R or +M) and negative resonance effect (-R or -M). **Positive resonance effect or electron donating / releasing resonance effect (+ R effect) :** If the substituent group has a lone pair of electrons to donate to the attached π bond or cojugated system of π bonds, the effect is called +R effect. Group such as - OH, - OR, - $O^{\ominus}$, - NHR, - halogen, etc. having lone pair of electrons show +R effect. The +R effect increases electron density at certain positions in a molecule. Figure 14.11 shows how the +R effect in aniline increases the electron density at ortho and para positions.

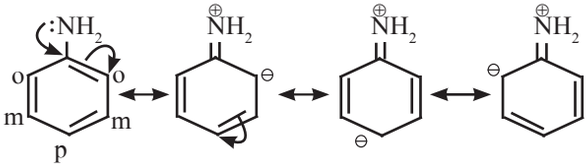


Fig. 14.11 : +R effect in aniline

Negative resonace effect or electron withdrawing resonance effect (-R effect) :

If the substituent group has a tendency to withdraw electrons from the attached π bond or conjugated system of π bonds towards itself, the effect is called -R effect. Group such as -COOH, -CHO, -CO-, -CN, $-NO_2$, - COOR, etc. show -R effect. The -R effect results in developing a positive polarity at certain positions in a molecule. Figure 14.12 shows how -R effect in nitrobenzene develops positive polarity at the ortho and para positions.

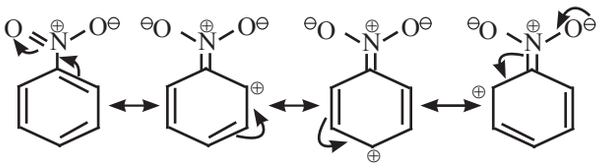
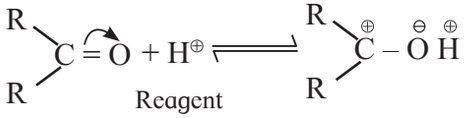


Fig. 14.12 : -R effect in aniline

14.6.7 Electromeric effect : This is a temporary electronic effect exhibited by multiple-bonded groups in the excited state in the presence of a reagent. When a reagent approaches a multiple bond, the electron pair gets completely shifted to one of the multiply bonded atoms, giving a charged separated structure. For example :



This effect is temporary and disappears when the reagent is removed from the reacting system.

14.6.8 Hyperconjugation :

Hyperconjugation is **a permanent electronic effect** explains stability of a carbocation, free radical or alkene. It is delocalization of σ (sigma) electrons of a C - H bond of an alkyl group directly attached to a carbon atom which is part of an unsaturated system or has an empty p- orbital or a p - orbital with an unpaired electron (see Fig. 14.13).

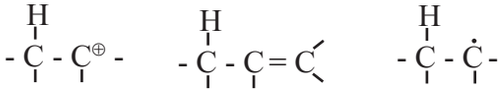


Fig. 14.13 Species stabilized by hyperconjugation

Let us consider ethyl cation ($CH_3\overset{\oplus}{C}H_2$). Here the positively charged carbon atom with an empty p -orbital has an adjacent methyl group, that is an α - (alpha) methyl group. One of the C-H bonds of this α methyl group is in allignment with the empty p-orbital. The σ electrons of this C-H bond or delocalized into the empty p -orbital and thereby stabilize the cation (see Fig. 14.14).

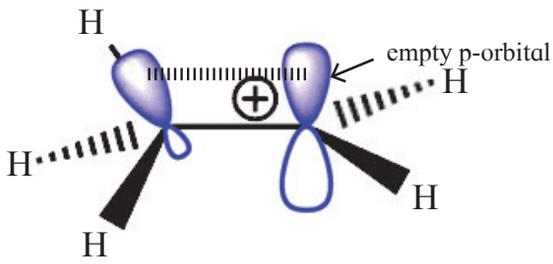
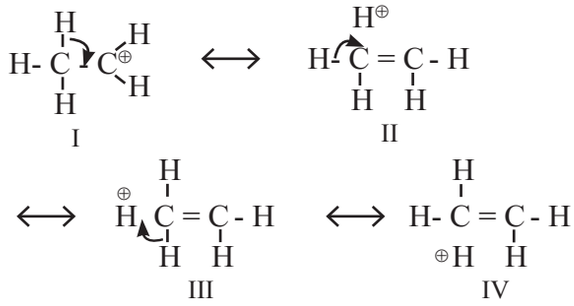
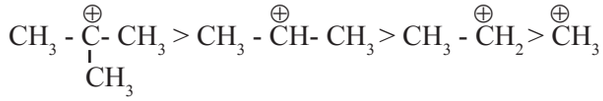


Fig. 14.14 Hyperconjugation in ethyl carbocation

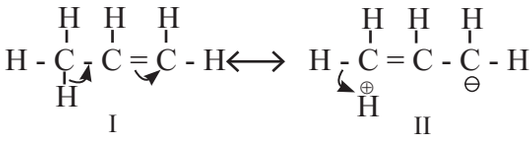
Hyperconjugation is, thus a σ-π conjugation.



The contributing structures II, III and IV involving delocalization of σ electrons of C-H bond shows no covalent bond between carbon and one of the α-hydrogens. Hyperconjugation is, therefore, called **'no bond resonance'**. More the number of such α–hydrogens (that is, hydrogen on the α- carbon), more are the no bond resonance structures and more is the stability. The relative stability of carbocations, therefore decreases in the order :



Let us now look at propene which has a methyl group attached to C = C. Delocalization of electrons by hyperconjugation in propene can be depicted as shown.



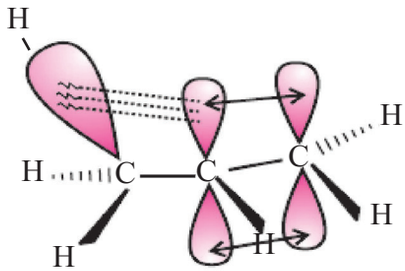


Fig. 14.15 : shows the orbital diagram of hyperconjugation in propene

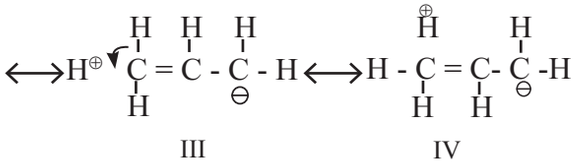


Figure 14.15 shows the orbital diagram of hyperconjugation in propene.

The effect of hyperconjugation is usually stronger than inductive effect.

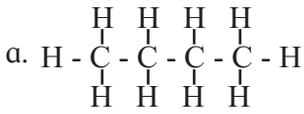
Internet my friend

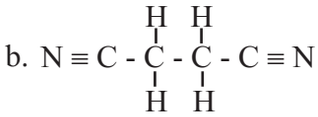
1. Basic principles of organic chemistry
   https://authors.library.caltech.edu/25034
2. Collect information about Isomerism

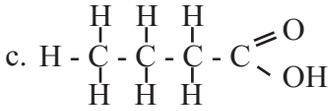
Exercises

1. Answer the following :

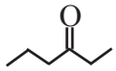
A. Write condensed formulae and bond line formulae for the following structures.

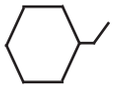
a. 

b. 

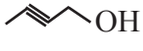
c. 

B. Write dash formulae for the following bond line formulae.

a. 

b. 

c. 

d. 

C. Write bond line formulae and condensed formulae for the following compounds

a. 3-methyloctane b. hept-2-ene

c. 2, 2, 4, 4- tetramethylpentane

d. octa-1,4-diene e. methoxyethane

D. Write the structural formulae for the following names and also write correct IUPAC names for them.

a. 5-ethyl-3-methylheptane

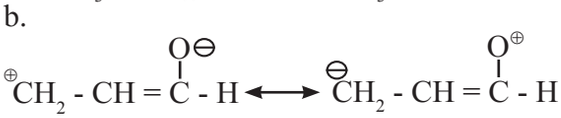
b. 2,4,5-trimethylthexane

c. 2,2,3-trimethylpentan-4-0l

E. Identify more favourable resonance structure from the following. Justify.

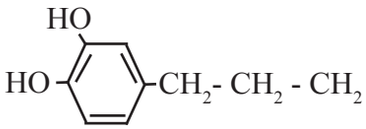
a. 

b.

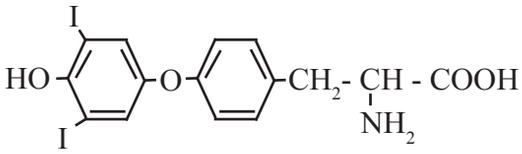


F. Find out all the functional groups present in the following polyfunctional compounds.

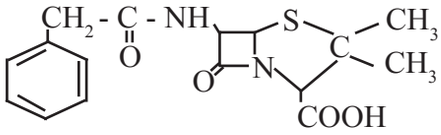
a. Dopamine a neurotransmitter that is deficient in Parkinson's disease.



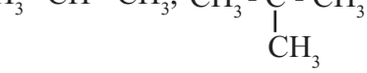
b. Thyroxine the principal thyroid hormone.



c. Penicillin G a naturally occuring antibiotic



G. Find out the most stable species from the following. Justify.

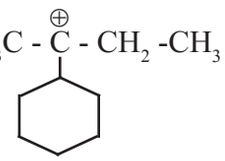
a. $\dot{C}H_3$, $CH_3 - \dot{C}H - CH_3$, 

b. $\overset{\ominus}{C}H_3$, $\overset{\ominus}{C}H_2Br$, $\overset{\ominus}{C}Br_3$

c. $\overset{\oplus}{C}H_3$, $\overset{\oplus}{C}H_2Cl$, $\overset{\oplus}{C}Cl_3$

H. Identify the α - carbons in the following species and give the total number of α-hydrogen in each.

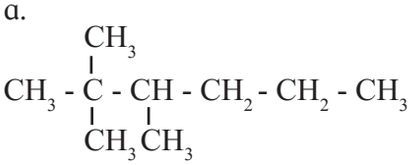
a. $CH_3 - CH_2 - \overset{\oplus}{C}H - CH_2 - CH_3$

b. 

c. $CH_2 = CH - CH_2 - CH_3$

I. Identify primary, secondary, tertiary and quaternary carbon in the following compounds.

a.



b.

2. Match the pairs

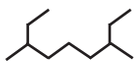
Column 'A'	Column 'B'
i. Inductive effect	a. delocalisation of π electrons
ii. Hyperconjugation	b. displacement of π electrons
iii. Resonance effect	c. delocalisation of σ electrons
	d. displacement of σ electrons

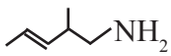
3. What is meant by homologous series ? Write the first four members of homologous series that begins with

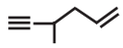
A. CH_3CHO B. H-C≡C-H

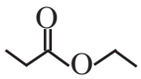
Also write down their general molecular formula.

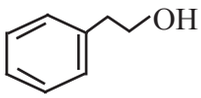
4. Write IUPAC names of the following

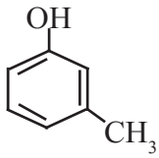
A. 

B. 

C. 

D. 

E. 

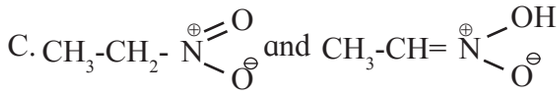
F. 

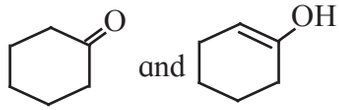
5 Find out the type of isomerism exhibited by the following pairs.

A. CH_3-CH_2-NH-CH_2-CH_3
and CH_3- NH - CH_2 - CH_2 - CH_3

B. CH_3-CH(OH)- CH_2 -CH_3 and

CH_3- CH_2- O - CH_2 - CH_3

C. 

D. 

6. Draw resonance srtuctures of the following :

A. Phenol B. Benzaldehyde
C. Buta-1,3-diene D. Acetate ion

7. Distinguish :

A. Inductive effect and resonance effect
B. Electrophile and nucleophile
C. Carbocation and carbanion
D. Homolysis and heterolysis

8. Write true or false. Correct the false stament

A. Homolytic fission involves unsymmetrical breaking of a covalent bond.
B. Heterolytic fission results in the formation of free radicals.
C. Free radicals are negatively charged species
D. Aniline is heterocyclic compound.

9. Phytane is naturally occuring alkane produced by the alga spirogyra and is a constituent of petroleum. The IUPAC name for phytane is 2,6,10,14-tetramethylhexadecane. Write zig-zag formula for phytane. How many primary, secondary, tertiary and quaternary carbons are present in this molecule.

10. Observe the following structures and answer the questions given below.

(i) CH_3 - CH_2 - CH_2 - CHO

(ii) CH_3 - CH(CHO) - CH_3

a. What is the relation between (i) and (ii) ?
b. Write IUPAC name of (ii).
c. Draw the functional group isomer of (i).

11. Observe the following and answer the questions given below

$CH_3 - CH_3 \xrightarrow{\text{U. V. light}} \dot{C}H_3 + \dot{C}H_3$

a. Name the reactive intermediae produced

b. Indicate the movement of electrons by suitable arrow to produce this intermediate

c. Comment on stability of this intermediate produced.

12. An electronic displacement in a covalent bond is represented by following noation.

$CH_3 \overset{\delta\oplus}{\rightarrow} CH_2 \overset{\delta\oplus}{\rightarrow} Cl^{\delta\ominus}$

A. Identify the effect

B. Is the displacement of electrons in a covalent bond temporary or permanent.

13. Draw all the no-bond resonance structures of isopropyl carbocation.

14. A covalent bond in tert-butylbromide breaks in a suitable polat solvent to give ions.

A. Name the anion produced by this breaking of a covalent bond.

B. Indicate the type of bond breaking in this case

C. Comment on geometry of the cation formed by such bond cleavage.

15. Choose correct options

A. Which of the following statements are true with respect to electronic displacement in covalent bond ?

a. Inductive effect operates through π bond

b. Resonance effect operates through σ bond

c. Inductive effect operates through σ bond

d. Resonance effect operates through π bond

i. a. and b ii. a and c

iii. c and d iv. b and c

B. Hyperconjugation involves overlap of ..... orbitals

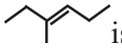
a. σ – σ b. σ –p

c. p – p d. π – π

C. Which type of isomerism is possible in $CH_3CHCHCH_3$?

a. Position b. Chain

c. Geometrical d. Tautomerism

D. The correct IUPAC name of the compound  is .....

a. hept-3-ene

b. 2-ethylpent-2-ene

c. hex-3-ene

d. 3-methylhex-3-ene

E. The geometry of a carbocation is .....

a. linear b. planar

c. tetrahedral d. octahedral

F. The homologous series of alcohols has general molecular formula .....

a. $C_nH_{2n+1}OH$ b. $C_nH_{2n+2}OH$

c. $C_nH_{2n-2}OH$ c. $C_nH_{2n}OH$

G. The delocaalization of electrons due to overlap between p-orbital and sigma bond is called

a. Inductive effect

b. Electronic effect

c. Hyperconjugation

d. Resonance

Activity :

Construct models of different types of organic compounds. Explain each compound in class.

15. Hydrocarbons

Can you recall?

1. What are hydrocarbons?
2. Write structural formulae of the following compounds : propane, ethyne, cyclobutane, ethene, benzene.

The compounds which contains carbon and hydrogen as the only elements are called hydrocarbons.

Hydrocarbons can be **open chain** or **cyclic**. In accordance with presence or absence of carbon-carbon multiple bond (C=C and/ or C≡C) the hydrocarbons are called **unsaturated** or **saturated**. Cyclic unsaturated hydrocarbon can be either **aromatic** or **nonaromatic** (Fig. 15.1).

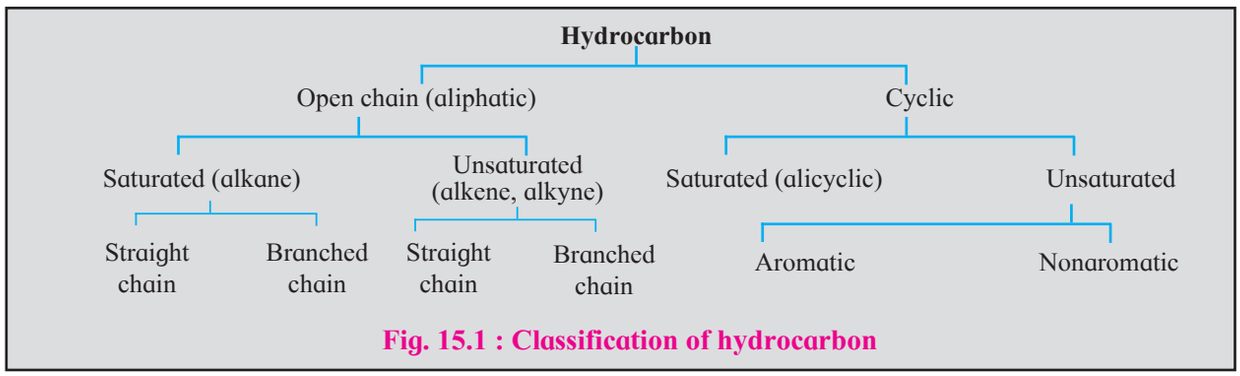


Fig. 15.1 : Classification of hydrocarbon

Do you know ?

Why are alkanes called paraffins?
Alkanes contain only carbon-carbon and carbon-hydrogen single covalent bonds. They are chemically less reactive and do not have much affinity for other chemicals. Hence they are called paraffins.

15.1 Alkanes

Alkanes are aliphatic saturated hydrocarbons containing carbon-carbon and carbon-hydrogen single covalent bonds. You have learnt in Chapter 14 that alkanes have general formula C_nH_{2n+2} where 'n' stands for the number of carbon atoms in the alkane molecule.

15.1.1 Isomerism in alkanes

Alkanes with more than three carbon atoms generally exhibit, structural isomerism and in particular, the chain isomerism (refer to section 14.5.1)

Internet my friend

Collect information about Hydrocarbon

Figure 15.2 shows IUPAC and common names of stuctural isomers of C_4H_{10} and C_5H_{12}.

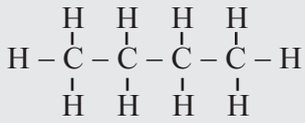
The number of possible structural isomers increases rapidly with the increase in the number of carbon atoms. (See the Table 15.1).

Table 15.1 : Alkanes and isomer number

Number of Carbon	Alkane	Number of isomers
1	Methane	No structural isomer
2	Ethane	No structural isomer
3	Propane	No structural isomer
4	Butane	Two
5	Pentane	Three
6	Hexane	Five

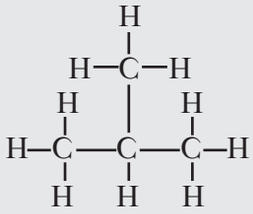
C_4H_{10}

i.



Butane (n-Butane)

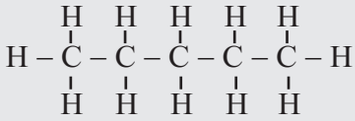
ii.



2-Methylpropane (Isobutane)

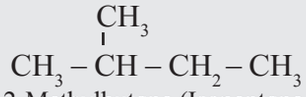
C_5H_{12}

i.



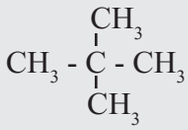
Pentane (n-Pentane)

ii.



2-Methylbutane (Isopentane)

iii.



2,2-Dimethylpropane (Neopentane)

Fig. 15.2 : Structural isomers of butane and pentane

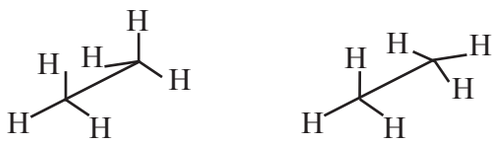
15.1.2 Conformations in alkanes : Alkanes have only single bonded atoms. You have learnt that a single covalent bond is formed by coaxial overlap of orbital and is called sigma (σ) bond (Refer to Chapter 5). As a direct consequence of coaxial overlap of orbitals, a sigma bond is cylindrically symmetrical and the extent of orbital overlap is unaffected by rotation about the single bond and therefore C-C bonds undergo rotation. The atoms bonded to one carbon of a C-C single bond change their relative position with reference to the atoms on the other carbon of that bond on rotation of that C-C single bond.

Use your brain power

1. Write the structures of all the chain isomers of the saturated hydrocarbon containing six carbon atoms.
2. Write IUPAC names of all the above structures

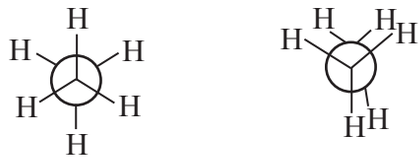
The resulting arrangements of the atoms in space about the C - C single bond are called conformations. Innumerable **conformations** result on complete rotation of a C - C single bond through 360°.

In chapter 14 you have learnt about **isomerism**. The phenomenon of existence of conformation is a type of **stereoisomerism**. In conformational isomerism the conformations (or **conformational isomers**) interconvert by rotation about a C - C single bond. Out of infinite **conformations of ethane** molecule two are extreme and called **staggered and eclipsed** conformation. They are represented by **Sawhorse formula** and **Newman projection formula** as shown in Fig. 15.3. Conformational isomerism in other alkanes is more complex.



Staggered Eclipsed

(a) Sawhorse formula



Staggered Eclipsed

(b) Newman Projection formula

Fig. 15.3 : Representation of staggered and eclipsed conformation of ethanes

15.1.3 Industrial preparation of alkanes

a. Industrial source : Crude petroleum and natural gas are the source of alkanes. Dead plants buried under earth billions of year ago got converted into crude oil under the high temperature and pressure conditions. The crude oil collected in dome shaped cavities under the earth surface, which we call oil wells. Alkanes are obtained by fractional distillation of crude oil in oil refineries.

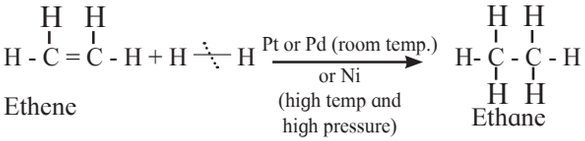
b. Methods of preparation of alkanes :

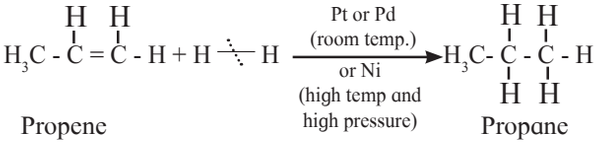
Can you recall?

- What is a catalyst ?
- What is addition reaction ?

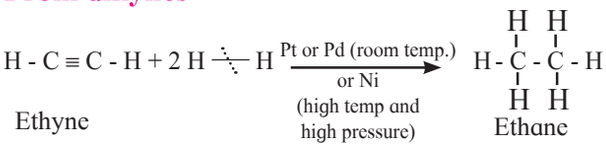
1. From unsaturated hydrocarbons : Catalytic hydrogenation of alkenes or alkynes with dihydrogen gas gives corresponding alkane. Finely divided powder of platinum (Pt) or palladium (Pd) catalyse the hydrogenation of alkenes and alkynes at room temperature. Relatively high temperature and pressure are required with finely divided nickel as the catalyst.

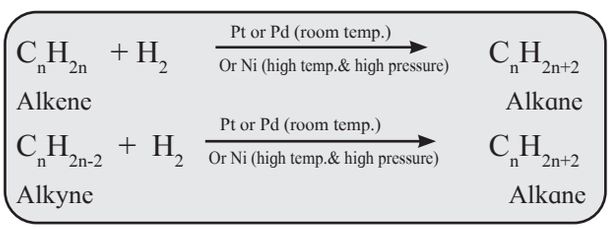
From alkenes





From alkynes





Try this

Transform the following word equation into balanced chemical equation and write at least 3 changes that occur at molecular level during this chemical change.

2-Methylpropene+Hydrogen $\xrightarrow{\text{catalyst}}$ Isobutane

2. From alkyl halides

a. By reduction of alkyl halides : Alkyl halides on reduction with zinc and dilute hydrochloric acid form alkanes. The reduction of alkyl halides is due to nascent hydrogen obtained from the reducing agent Zn and dilute HCl.

$$CH_3 - I + 2[H] \xrightarrow{Zn,\ HCl} CH_4 + HI$$

Methyl iodide — Nascent — Methane

$$CH_3 - CH_2 - Br + 2[H] \xrightarrow{Zn,\ HCl} 2\,CH_3 - CH_3 + HBr$$

Ethyl bromide — Nascent — Ethane

b. By using reactive metal : In 19th century alkyl halides were transformed to alkane having double the number of carbons by Wurtz coupling reaction using the reactive metal sodium.

$$CH_3 - Br + 2Na + Br - CH_3 \xrightarrow{\text{dry ether}} CH_3 - CH_3 + 2NaBr$$

Later bettter methods using metals such as Mg, Li were developed. Grignard reaction is one of the new methods widely employed for preparation of alkanes.

Alkyl magnesium halides (Grignard reagent) are obtained by treating alkyl halides with dry metal magnesium in the presence of dry ether. These on treatment with water give alkanes.

$$R - X + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

Alkyl halide — Alkyl magnesium halide

$$R - Mg - X + H - O - H \xrightarrow{\text{dry ether}} R - H + MgX(OH)$$

Alkane

$$CH_3 - Mg - I + H - O - H \xrightarrow{\text{dry ether}} CH_3 - H + MgI(OH)$$

Methyl magnesium iodide — Methane

Do you know ?

Prepartion of Grignard reagent is an exothermic reaction. Hence no heating is required. In this reaction :

i. Magnesium metal gradually diappears.

ii. Magnesium atoms gets bonded to the same carbon that previously held halogen.

iii. Alkyl group remains as it is or intact during the preparation grignard reagent.

iv. Dry and inert conditions are to be maintained during Grignard reaction to prevent any reaction with moisture.

15.1.4 Physical properties of alkanes

i. Polarity : The electronegativity of carbon and hydrogen is nearly the same. C-H and C-C bonds are non-polar covalent bonds and alkanes are, thus, nonpolar. The forces which hold non-polar molecules together are the van der Waals forces. Those are usually weak. Larger the surface area of molecules, stronger are such intermolecular van der Waals forces.

The intermolecular forces are relatively stronger in straight chain alkanes than in branched alkanes (See Fig. 15.4).
Therefore straight chain alkanes have higher melting and boiling points.

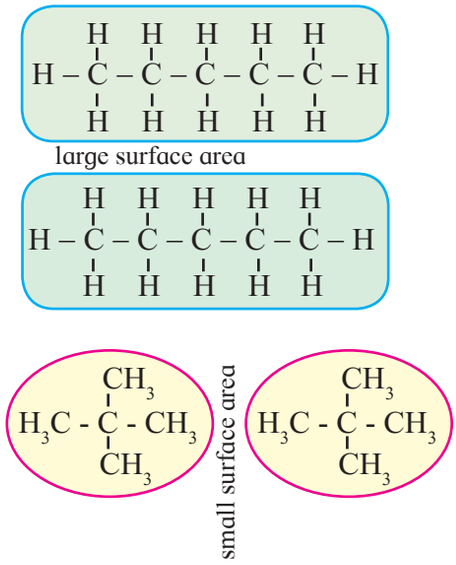


Fig. 15.4 : Relative surface area of straight chain and branched alkanes

Branched alkanes have lower melting and boiling points. Intermolecular forces are overcome partly during melting process and completely during boiling process. Table 15.2 shows the melting and boiling points of some alkanes. Alkanes are colourless and odourless. At room temperature, the first four alkanes are gases, next alkanes having 5 to 17 carbons are liquids and carbons 18 onwards are solids.

Use your brain power

Why are alkanes insoluble in water and readily soluble in organic solvents like chloroform or ether ?

Table 15.2 : Melting and Boiling points in alkanes

Molecular formula	Name	Molecular mass/u	b.p. (K)	m.p. (K)
CH_4	Methane	16	111.0	90.5
C_2H_6	Ethane	30	184.4	101.0
C_3H_8	Propane	44	230.9	85.3
C_4H_{10}	Butane	58	272.4	134.6
C_4H_{10}	2-Methylpropane	58	261.0	114.7
C_5H_{12}	Pentane	72	309.1	143.3
C_5H_{12}	2-Methylbutane	72	300.9	113.1
C_5H_{12}	2,2-Dimethylpropane	72	282.5	256.4
C_6H_{14}	Hexane	86	341.9	178.5

15.1.5 Chemical properties of alkanes :

Alkanes are relatively unreactive towards acids, bases, oxidizing and reducing agents. They undergo the following reactions under specified conditions.

1. Halogenation of alkanes : The reactions in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms are known as **substitution reactions**. Substitution of H atoms of alkanes by X (halogen, X= Cl, Br, I and F) atom is called **halogenation of alkanes**. Alkanes react with halogens in presence of UV light or diffused sunlight or at higher temperature (573 To 773 K) to give mixture of alkyl halides.

Chlorination of methane :

$$CH_4 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} CH_3Cl + HCl$$

Methane, Chlorine → Chloromethane (Methyl chloride), Hydrogen chloride

$$CH_3Cl + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} CH_2Cl_2 + HCl$$

Chloromethane → Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} CHCl_3 + HCl$$

Dichloromethane → Trichloromethane

$$CHCl_3 + Cl_2 \xrightarrow[\text{or } \Delta]{\text{UV light}} CCl_4 + HCl$$

Trichloromethane → Tetrachloromethane

Tetrachloromethane is a major product when excess of chlorine is used. Chloromethane is obtained as major product when excess of methane is employed. The reactivity of halogens toward alkanes follows the order

$F_2 > Cl_2 > Br_2 > I_2$.

The ease of replacement of hydrogen atoms from the carbon is in the order of

$3^0 > 2^0 > 1^0$.

For example,

$$CH_3-CH_2-CH_3 \xrightarrow[\text{UV light}]{Cl_2} CH_3-CH_2-CH_2-Cl + CH_3-\underset{Cl}{CH}-CH_3$$

Propane → 1-Chloropropane (45%) + 2-Chloropropane (55%)

$$CH_3-\underset{CH_3}{CH}-CH_3 \xrightarrow[\text{UV light}]{Cl_2} CH_3-\underset{CH_3}{CH}-CH_2-Cl + CH_3-\underset{\underset{Cl}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_3$$

2-Methylpropane → 1-Chloro-2-methylpropane (36%) + 2-Chloro-2-methylpropane (64%)

Bromination gives corresponding bromides, but in different proportions. For example,

$$CH_3-CH_3 \xrightarrow[\text{UV light}]{Br_2} CH_3-CH_2-Br$$

Ethane → Bromoethane

$$CH_3-CH_2-CH_3 \xrightarrow[\text{UVlight}]{Br_2} CH_3-CH_2-CH_2-Br + CH_3-\underset{Br}{CH}-CH_3$$

Propane → 1-Bromopropane (3%) + 2-Bromopropane (97%)

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{UV light}]{Br_2} CH_3-CH_2-CH_2-CH_2-Br + CH_3-CH_2-\underset{Br}{CH}-CH_3$$

Butane → 1-Bromobutane(2%) + 2-Bromobutane (98%)

$$CH_3-\underset{CH_3}{CH}-CH_3 \xrightarrow[\text{UV light}]{Br_2} CH_3-\underset{CH_3}{CH}-CH_2-Br + CH_3-\underset{\underset{Br}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_3$$

2-Methylpropane → 1-Bromo-2-methylbutane (trace) + 2-Bromo-2-methylpropane (over 99%)

In bromination, there is high degree of selectivity as to which hydrogen atoms are replaced. Halogenation of alkanes follows the free radical mechanism. Homolysis of halogen molecule (X_2) generates halogen atoms, that is, halogen free radicals. The mechanism of the first step of chlorination of methane is shown below :

$$Cl-Cl \xrightarrow[\text{homolysis}]{\text{UV}} \dot{Cl} + \dot{Cl}$$

(initiation)

$$H_3C-H + \dot{Cl} \longrightarrow H_3\dot{C} + H-Cl$$

$$H_3\dot{C} + Cl-Cl \longrightarrow H_3C-Cl + \dot{Cl}$$

(propagation)

Remember

1. Depending upon which hydrogen atom is replaced, a number of isomeric products can be formed from alkane. For example, n-Butane and isobutane yield two isomers each.
2. Halogenation an alkane yields a mixture of all possible isomeric products, indicating all the hydrogen atoms are susceptible to substitution.

2. Combustion : Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of a large amount of heat. That is why alkanes are good fuels.

$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$;

Methane

$\Delta_C H^0 = -\ 890\ kJ\ mol^{-1}$

$C_4H_{10} + 13/2\ O_2 \longrightarrow 4\ CO_2 + 5H_2O$;

Butane

$\Delta_C H^0 = -\ 2875.84\ kJ\ mol^{-1}$

A representative combustion equation for alkane is

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow n\ CO_2 + (n+1)\ H_2O + Heat$$

Can you recall?

What is the product which is poisonous and causes air pollution formed by incomplete combustion of alkane ?

3. Pyrolysis : Alkanes on heating at higher temperature in absence of air decompose to lower alkanes, alkenes and hydrogen, etc. This is known as **pyrolysis or cracking**.

$$C_6H_{14} \xrightarrow{773\ K} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$

4. Reforming : Straight chain alkanes containing 6 to 10 carbon atoms are converted to benzene and its homologues on heating under 10 to 20 atm pressure at about 773 K in the presence of V_2O_5, Cr_2O_3 ,Mo_2O_3 etc. supported over alumina. The reaction involves simultaneous dehydrogenation and cyclization. This reaction is known as **aromatization or reforming** .

$H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

n-Hexane

$$\xrightarrow[773K,\ 10\text{-}20\ atm]{V_2O_5} \text{C}_6\text{H}_6 + 4H_2$$

Benzene

This process is used in refineries to produce high quality gasoline (the fuel used in automobiles).

Use your brain power

Name the alkane from which methyl benzene is obtained by reforming?

Collect the information of CNG and LPG with reference to the constituents and the advantages of CNG over LPG.

15.1.6 Uses of alkanes :

1. First four alkanes are used as a fuel mainly for heating and cooking purpose. for example, LPG and CNG.
2. CNG, petrol, diesel are used as fuels for automobiles.
3. Lower liquid alkanes are used as solvent.
4. Alkanes with more than 35 C atoms (tar) are used for road surfacing.
5. Waxes are high molecular weight alkanes. They are used as lubricants.They are also used for the preparation of candles and carbon black that is used in manufacture of printing ink, shoe polish, etc.

Can you recall?

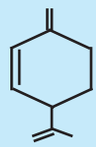
- What are alkenes?
- Calculate the number of sigma (σ) and pi (π) bonds in 2-Methylpropene ?
- Write structural formula of pent-2-ene.

15.2 Alkenes : Alkenes are unsaturated hydrocarbons containing at least one carbon-carbon double bond. Alkenes with one carbon-carbon double bond, contain two hydrogen atoms less than corresponding alkanes.They have general formula C_nH_{2n}.where n= 2,3,4... etc. You have also learnt about the IUPAC names of alkenes in Chapter 14.

Do you know ?

1. Alkenes are also known as olefins, because the first member ethylene or ethene reacts with chlorine to form oily substance.
2. The aliphatic unsaturated hydrocarbon containing two or three carbon-carbon double bonds are called alkadienes and alkatrienes, respectively. for example,

$H_2C = \overset{CH_3}{\overset{|}{C}} - CH = CH_2$ Methylbuta-1,3-diene (Isoprene)



β-Phellandrene (oil of eucalyptus)

15.2.1 Isomerism in alkenes : Alkenes with more than three carbon atoms show both **structural isomerism** and **geometrical isomerism**.

i. Structural isomerism : Alkenes with molecular formula C_4H_8 is butene. The structural formulae for C_4H_8 can be drawn in three diffferent ways :

$H_2\overset{1}{C} = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H_3$

(I) But-1-ene (Chain of 4 carbon atoms)

$H_3\overset{1}{C} - \overset{2}{C}H = \overset{3}{C}H - \overset{4}{C}H_3$

(II) But-2-ene (Chain of 4 carbon atoms)

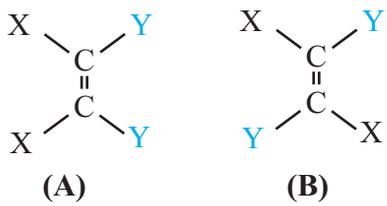
$H_2\overset{1}{C} = \overset{2}{\overset{|}{C}} - \overset{3}{C}H_3$ (CH_3 on C-2)

(III) 2-Methylprop-1-ene (Chain of 3 carbon atoms)

Structure I and III along with II and III are the examples of chain isomerism. They differ in carbon chain length. Structure I and II are the examples of position isomerism because they differ in the position of double bond in the same carbon chain.

ii. Geometrical isomerism

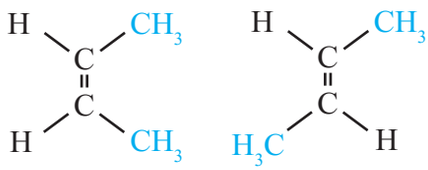
The isomerism which arises due to the difference in spatial arrangement of atoms or groups about doubly bonded carbon (C=C) atoms is called *geometrical isomerism*. If the two atoms or groups bonded to each end of the C=C double bond are different, then molecule can be represented by two different special arrangements of the groups as follows :



(A) **(B)**

In structure (A), two identical atoms or groups lie on the same side of the double bond. **The geometrical isomer in which two identical or similar atoms or groups lie on the same side of the double bond is called *cis-isomer*.**

In structure (B), two identical atoms or groups lie on the opposite side of the double bond. **The geometrical isomer in which two identical or similar atoms or groups lie on the opposite side of the double bond is called trans-isomer.** Due to different arrangement of atoms or groups in space, these isomers differ in their physical properties like melting point, boiling point, solubility etc. Geometrical or cis-trans isomers of but-2-ene are represented as :



cis-But-2-ene (b.p. = 277 K)

trans- But-2-ene (b.p. = 274 K)

Do you know ?

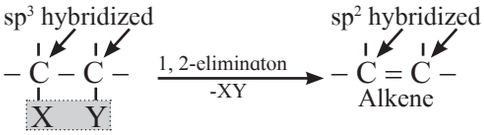
1. No terminal alkenes i.e. those with $C=CH_2$ unit can exist as cis- and trans-isomers.
2. No 1,1-disubstituted alkenes i.e. those with $C = CR_2$ unit can exist as cis- and trans -isomers.
3. Alkenes with general formulae $RCH=CHR$, $R_1R_2C = CR_1R_2$, $R_1CH=CR_1R_2$, $R_1CH=CR_2R_3$, $R_1CH=CHR_2$ and $R_1R_2C= CR_3R_4$ exibit cis-trans isomerism.

15.2 Preparation of alkenes

a. Industrial sources : The most important alkenes for chemical industry are ethene, propene and buta-1,3-diene. Alkenes containing upto four carbon atoms can be obtained in pure form from the petroleum products. Ethene is produced from natural gas and crude oil by cracking.

b. Methods of preparation of alkenes

(I) Elimination reactions : (1,2 -elimination) The reactions in which two atoms or groups are eliminated or removed from adjacent carbon atoms are called **1,2 - elimination reactions**.



Remember

1. The carbon - carbon double bond can be generated from a carbon -carbon single bond by elimination reaction.
2. During elimination reaction sp^3 carbon atom changes to sp^2 carbon atom.

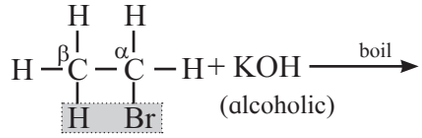
Some elimination reactions useful to prepare alkenes are described below.

i. Dehydrohalogenation of alkyl halides

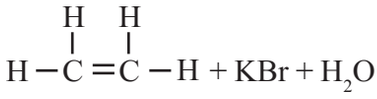
Dehydrohalogenation means removal of hydrogen (H) atom and halogen (X) atom from adjacent carbon atoms. The carbon carrying X is called α-carbon atom.

The hydrogen atom from adjacent carbon called β-carbon atom, is removed and the reaction is known as β-elimination.

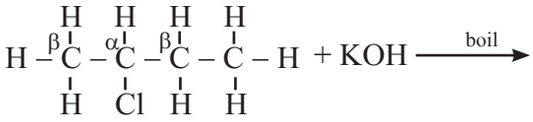
Dehydrohalogenation suffers from the disadvantage that -H can be eliminated from the carbon on either side of the α-carbon bearing the -X. When an alkyl halide is boiled with a hot concentrated alcoholic solution of a strong base like KOH or NaOH, alkene is formed with removal of water molecule.



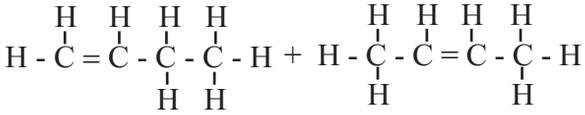
Bromoethane



Ethene



2-Chlorobutane alcoholic



But-1-ene (20%) But-2-ene (80%)

$+ KBr + H_2O$

In dehydrohalogenation of 2-Chlorobutane, but-2-ene (disubstituted alkene) is the preferred product because it is formed faster than but-1-ene (monosubstituted alkene). This is in accordance to with Saytzeff rule.

Saytzeff rule : *In dehydrohalogenation the preferred product is the alkene that has the greater number of alkyl groups attached to doubly bonded carbon atoms.*

The ease of dehydrohalogenation of alkyl halides accordingly is in the order $3^0 > 2^0 > 1^0$

The ease of formation of alkenes :

$R_2C = CR_2 > R_2C= CHR > R_2C = CH_2$, $RCH=CHR > RCH=CH_2$

The stability of alkenes :

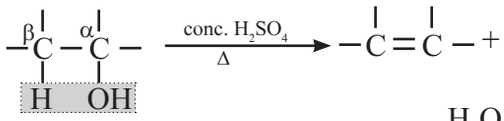
$R_2C = CR_2 > R_2C= CHR > R_2C = CH_2$, $RCH=CHR > RCH=CH_2 > CH_2 = CH_2$

Can you recall?

- What are alcohols ?
- What is a dehydration reaction?
- What is a catalyst ?

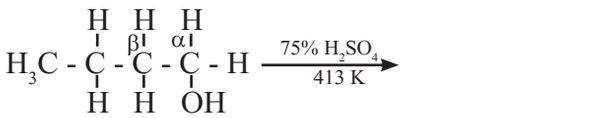
ii. Dehydration of alcohols : Alcohols on heating with sulphuric acid form alkenes with elimination of water molecule. The reaction is known as catalyzed dehydration of alcohols. The exact conditions of dehydration depend upon the alcohol.

Dehydration of alcohol is an example of β-elimination since OH group from α-carbon along with a H atom from β-carbon atom is removed.

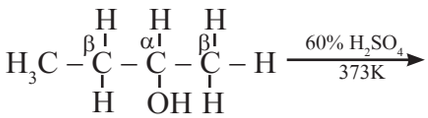


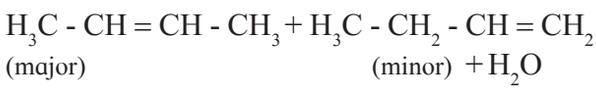
Alcohol Alkene

The ease of dehydration of alcohols is in the order $3^0 > 2^0 > 1^0$

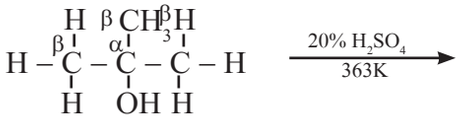


Butan-1-ol But-1-ene (main product)

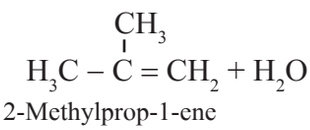




(major) (minor)



2-Methylpropan-2-ol



2-Methylprop-1-ene

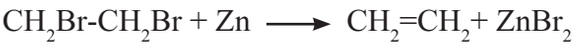
Can you tell?

1. Explain by writing a reaction, the main product formed on heating 2-methylbutan-2-ol with concentrated sulphuric acid.
2. Will the main product in the above reaction show geometrical isomerism?

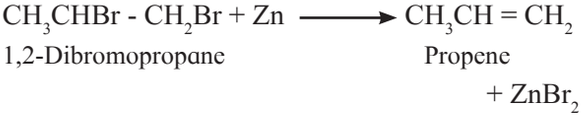
iii. By dehalogenation of vicinal dihalides :

Removal of two halogen atoms from adjacent carbon atoms is called dehalogenation. The dihalides of alkane in which two halogen atoms are attached to adjacent carbon atoms are called vicinal dihalides. Vicinal dihalides on heating with zinc metal form alkenes.

Vicinal dihalide Alkene



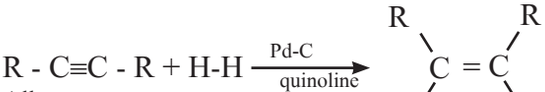
1,2-Dibromoethane Ethene



1,2-Dibromopropane Propene

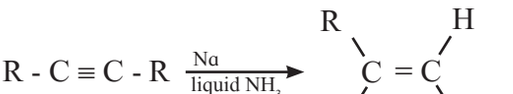
(II) Addition reactions : By partial reduction of alkynes (or controlled hydrogenation of alkynes) :

The C ≡ C triple bond of alkynes can be partially reduced to a C = C double bond with calculated quantity of dihydrogen in presence of Lindlar's catalyst (palladised charcoal deactivated partially with quinoline or sulfur compound). The *Cis* isomer is obtained by this method.



Alkyne cis-Alkene

Trans alkene is obtained from alkyne on reduction with sodium in liquid ammonia.



Alkyne trans-alkene

Table 15.3 : Melting point and boiling point of alkenes

Fornula	Name	Molecular mass (u)	b.p. (K)	m.p. (K)
$CH_2=CH_2$	Ethene	28	171	104
$CH_2 = CHCH_3$	Propene	42	225	88
$CH_2 =CHCH_2CH_3$	But-1-ene	56	267	--
$CH_2 = CH(CH_2)_2CH_3$	Pent-1-ene	70	303	--
$CH_2 =CH(CH_2)_3CH_3$	Hex-1-ene	84	337	135
cis $CH_3CH = CH\ CH_3$	cis-But-2-ene	56	277	134
trans $CH_3CH = CHCH_3$	trans-But-2-ene	56	274	167
$CH_2 = C(CH_3)_2$	Isobutylene	56	266	132

15.2.3 Physical properties of alkenes : Alkenes are nonpolar or weakly polar compounds those are insoluble in water, and soluble in non-polar solvents like benzene, ether, chloroform. They are less dense than water. From Table 15.3, it is clear that the boiling point of alkene rises with increasing number of carbons. Branched alkenes have lower boiling point than the corresponding straight chain alkane. The boiling point of alkene is very nearly the same as that of alkane with the same carbon skeleton.

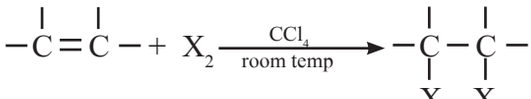
15.2.4 Chemical properties of alkenes :

Alkenes are more reactive than alkene due to the presence of pi (π) electrons. They undergo electrophilic addition reactions. The different reactions of alkenes are given below:

1. Addition of dihydrogen/hydrogenation (see section 15.1.4).

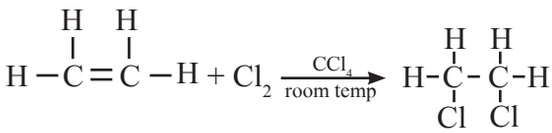
2. Addition of halogens/halogenation.

Alkenes are converted into the corresponding vicinal dihalides by addition of halogens ($X_2 = Cl_2$ or Br_2) .

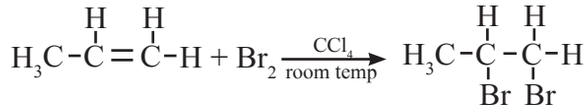


Alkene — Vicinal dihalide

Iodine generally fails to react.



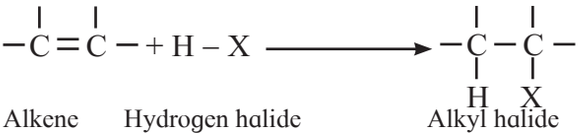
Ethene — 1,2-Dichloroethane



Propene — red brown — 1,2- Dibromopropane (Colourless)

Addition of bromine is useful test for detection C = C in unknown compounds. Red brown colour of bromine rapidly disappears in carbontetrachloride solution if a C = C double bond is present in the compound.

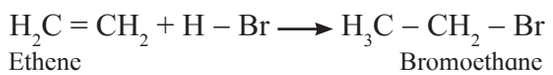
3. Addition of hydrogen halides/ hydrohalogenation : Addition of hydrogen halides (HX) like hydrogen chloride, hydrogen bromide and hydrogen iodide converts alkene into the corresponding alkyl halides.



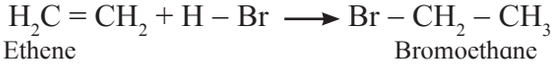
Alkene — Hydrogen halide — Alkyl halide

The order of reactivity of hydrogen halides is HI > HBr > HCl

Addition reaction of HBr to symmetrical alkenes : The addition of HBr to symmetrical alkenes yield only one product.

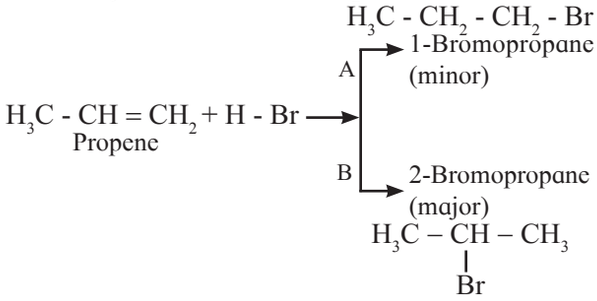


Ethene — Bromoethane



Ethene — Bromoethane

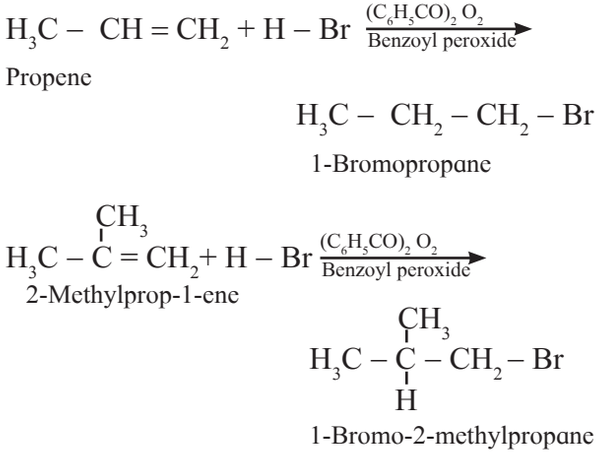
Addition reaction of HBr to unsymmetrical alkenes : Addition of HBr to unsymmetrical alkenes yield two isomeric products.



Experimentally it has been found that 2-Bromopropane is the major product. Russian chemist Markovnikov studied hydrohalogenation of a number of an unsymmetrical alkenes and formulated a geneneral rule (1869) as follows :

Markovnikov's rule : When an unsymmetrical reagent is added to unsymmetrical alkene, the negative part ($X^{\ominus}$) of the reagent gets attached to the carbon atom which carries less number of hydrogen atoms.

Anti- Markovnikov addition Or peroxide effect or Kharasch - Mayo effect : In 1933, M. S. Kharasch and F. R. Mayo discovered that the addition of HBr to unsymmetrical alkene in the presence of organic peroxide (R-O-O-R) takes place in the opposite orientation to that suggested by Markovnikov 's rule.

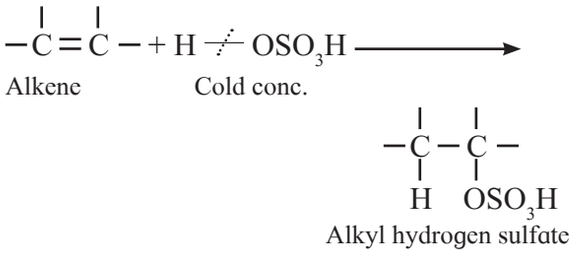


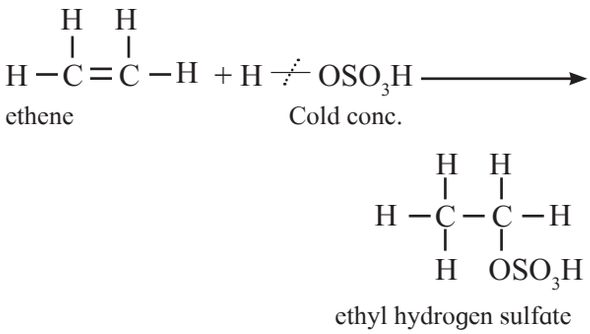
Remember

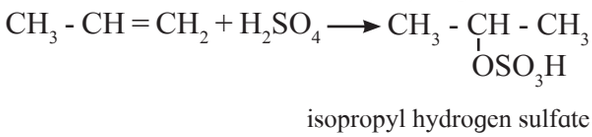
1. The orientation of addition of HBr to unsymmetrical alkene is determined by the presence or absence of peroxide.
2. The peroxide has no effect upon the addition of HCl and HI.

4. Addition of sulfuric acid

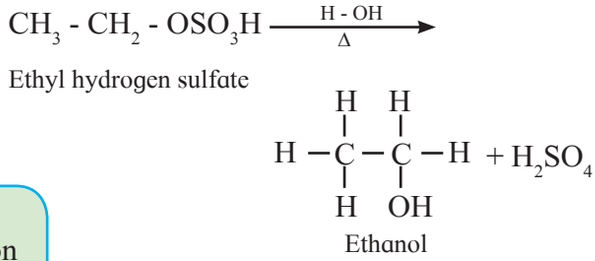
Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulfate ($ROSO_3H$). The addition takes place according to **Markovnikov's rule**.





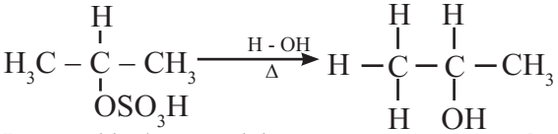


If alkyl hydrogen sulfate is diluted with water and heated, then an alcohol having the same alkyl group as the original alkyl hydrogen sulfate is obtained. This is an excellent method for the large scale manufacture of alcohols.



Internet my friend

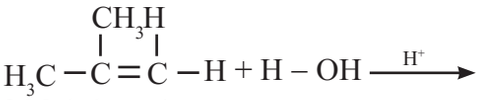
https://www.britanicacom>science>hydrocarbon



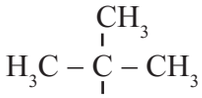
Isopropyl hydrogen sulphate propan-2-ol

$+ H_2SO_4$

Reactive alkenes on adding water molecules in the presence of concentrated sulphuric acid, form alcohol.The addition of water takes place according to **Markovnikov's rule**.This reaction is known as hydration of alkenes.



2-Methylprop-1-ene

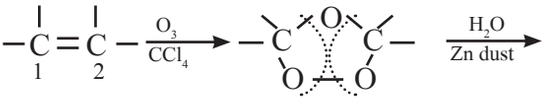


2-Methylpropan-2-ol

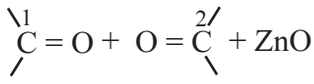
Can you tell?

Why are Propan-1-ol and 2-Methypropan-1-ol are not prepared by this method ?

5. Ozonolysis of alkenes : The C = C double bond gets cleaved on reaction with ozone followed by reduction. This overall process of formation of ozonide by reaction of ozone with alkene in the **first step** and then decomposing it to the carbonyl compounds by reduction in the **second step** is called ozonolysis.

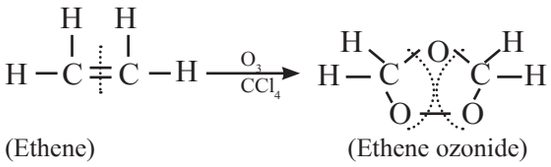


Alkene alkene ozonide

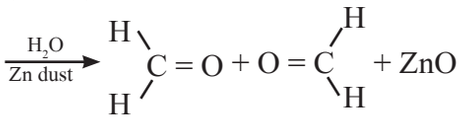


Carbonyl compounds

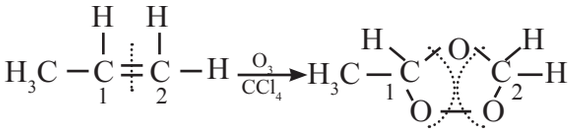
Ozone gas is passed into solution of the alkene in an inert solvent like carbon tetrachloride, unstable alkene ozonide is obtained. This is subsequently treated with water in the presence of a reducing agent zinc dust to form carbonyl comounds, namely, aldehydes and/or ketones .



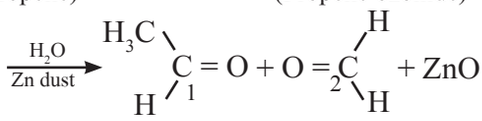
(Ethene) (Ethene ozonide)



(Formaldehyde) (Formaldehyde)



(Propene) (Propene ozonide)



(Acetaldehyde) (Formaldehyde)

Remember

1. In the cleavage products a carbonyl group (C =O) is formed at each of the original doubly bonded carbon atoms.
2. Knowing the number and arrangement of carbon atoms in these aldehydes and ketones produced, we can identify the structure of original alkene.
3. The role of zinc dust is to prevent the formation of hydrogen peroxide which oxidizes aldehydes to corresponding acids.
4. This reaction is used to locate the position and determine the number of double bonds in alkenes.

Use your brain power

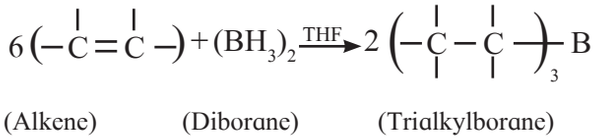
On ozonolysis an alkene forms the following carbonyl compounds. Draw the structure of unknown alkene from which these compounds are formed.

HCHO and $CH_3COCH_2CH_3$

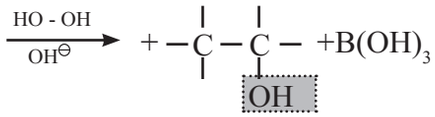
6. Hydroboration- oxidation of alkene

Alkenes with diborane in tetrahydrofuran (THF) solvent undergo hydroboration to form trialkylborane, which on oxidation with

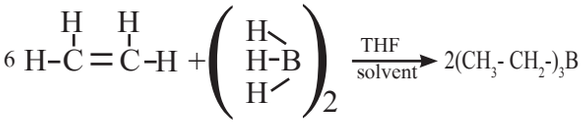
alkaline peroxide forms primary alcohol. The overall reaction gives **Anti-Markovnikov's** product from unsymmetrical alkenes



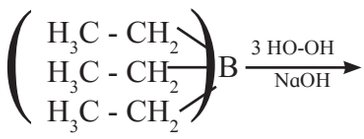
(Alkene) (Diborane) (Trialkylborane)



(Alcohol)

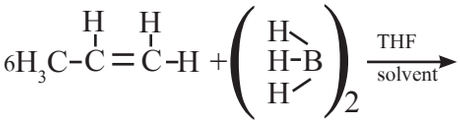


(Ethene) (Diborane)

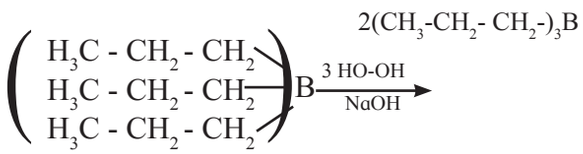


(Triethylborane)

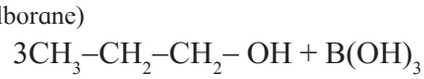
(Ethanol)



(Propene) (Diborane)



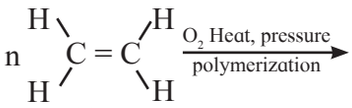
(Tri-n-propylborane)



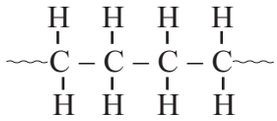
(Propan-1-ol)

7. Polymerization : The process in which large number of small molecules join together and form very large molecules with repeating units is called **polymerization**. The compound having very large molecules made of large number repeating small units is called **polymer** and the simple compound forming the repeating units in the polymer is called **monomer**.

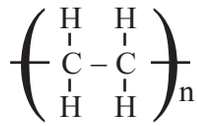
For example, ethene at high temperature and under high presssure interacts with oxygen, and undergoes polymerization giving high molecular weight polymer called polyethene.



(Ethene)
(Monomer)



Or



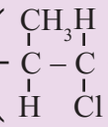
(Polyethene)
(Polymer)

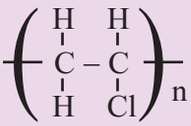
Here n represents the number of repeating units and is a large number.

Use your brain power

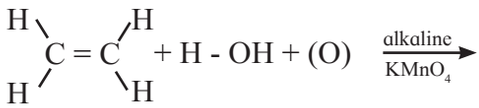
Write the structure of monomer from which each of the following polymers are obtained.

a. Teflon

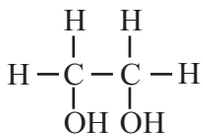
b. Polypropene 

c. Polyvinyl chloride 

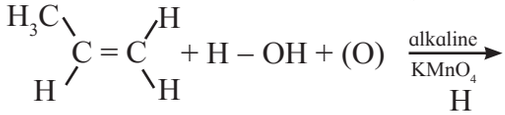
8. Hydroxylation : Alkenes react with cold and dilute alkaline potassium permanganate to form glycols.



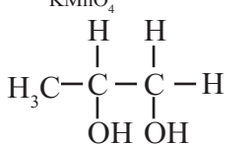
(Ethene)



(Ethane-1,2-diol)



(Propene)



(Propane-1,2-diol)

Hydroxylation of alkenes is the most important method for the synthesis of 1,2-diols (Glycols). During this reaction the purple colour of $KMnO_4$ disappears. Hence such reaction serves as qualitative test for detecting the presence of double bond in the compound under test. This is known as **Baeyer's test**.

9. Oxidation : Alkenes on oxidation with acidic $KMnO_4$ or acidic potassium dichromate form ketones and / or acids.

$$\underset{\text{(Prop-1-ene)}}{H_3C - CH = CH_2} \xrightarrow[(O)]{KMnO_4,\ H^{\oplus}} \underset{\text{(Ethanoic acid)}}{H_3C - \overset{O}{\overset{\|}{C}} - OH} + CO_2 + H_2O$$

$$\underset{\text{(2-Methylbut-2-ene)}}{H_3C - \overset{CH_3}{\overset{|}{C}} = CH - CH_3} \xrightarrow[(O)]{KMnO_4,\ H^{\oplus}} \underset{\text{Propan-2-one}}{H_3C - \overset{CH_3}{\overset{|}{C}} = O} + \underset{\text{Ethanoic acid}}{H_3C - \overset{O}{\overset{\|}{C}} - OH}$$

15.2.5 Uses of alkenes

1. Alkenes, are used as starting materials for preparation of alkyl halides, alcohols, aldehydes, ketones , acids etc.
2. Ethene and propene are used to manufacture polythene, polypropylene those find use in bags, toys, bottles, etc.
3. Ethene is used for artificial ripening of fruits, such as mangoes.

Can you tell?

- What are aliphatic hydrocarbons?
- Compare the proportion of carbon and hydrogen atoms in ethane, ethene and ethyne. Which compound is most unsaturated with hydrogen ?

15.3 Alkynes : Alkynes are aliphatic unsaturated hydrocarbons containing at least one C ≡ C.The number of hydrogen atoms is still less in alkynes as compared to alkenes. Their general formula is C_nH_{2n-2} . Table 15.4 shows names and formulae of lower alkynes.

15.3 Isomerism in alkynes : Alkynes show position isomerism which is a type of structural isomerism. For example 1-butyne and 2-butyne. 1-Alkynes are also called terminal alkynes.

Table 15.4 : Lower alkynes

n	Molecular formula	Structural formula and Common name	IUPAC name
2	C_2H_2	H-C ≡ C-H Acetylene	Ethyne
3	C_3H_4	CH_3-C≡ CH Methyl acetylene	Propyne
4	C_4H_6	CH_3-CH_2-C≡CH Ethyl acetylene	But-1-yne
5	C_4H_6	CH_3 - C ≡ C - CH_3 Dimethyl acetylene	But-2-yne

Do you know ?

1. Simplest alkyne is ethyne which is known as acetylene.
2. The carbon-carbon triple bond is a functional group.
3. The aliphatic unsaturated hydrocarbons containing two or three carbon-carbon triple bonds are called alkadiynes and alkatriynes, respectively.
4. Cicutoxin from poisonous plants 'water hemlock'.

HO - $(CH_2)_3$ - C ≡ C - C ≡ C - $(C_{10}H_{14})$ -OH

15.3.2 Preparation of alkynes

a. Industrial sources :

i. Ethyne is industrially prepared by controlled, high temperature partial oxidation of methane.

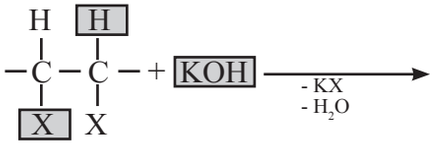
$$\underset{\text{Methane}}{6CH_4} + 2O_2 \xrightarrow{1773K} \underset{\text{Ethyne}}{2H - C \equiv C - H} + 2\,CO_2 + 10\,H_2$$

ii. From calcium carbide : Industrially the alkyne ethyne is prepared by reaction of calcium carbide with water.

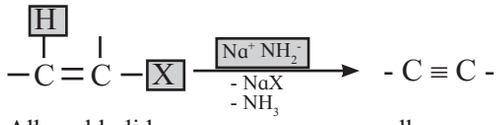
$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

b. Methods of preparation of alkynes

1. By dehydrohalogenation of vicinal dihalides : Removal of H and X from adjacent carbon atoms is called dehydrohalogenation. Vicinal dihalides react with alcoholic solution of potassium hydroxide to form alkenyl halide which on further treating with sodamide forms alkyne.

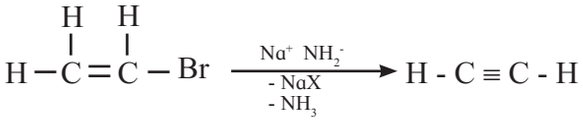


Vicinal dihalide (Alcoholic)

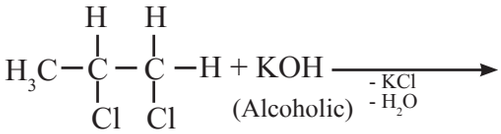


Alkenyl halide alkyne

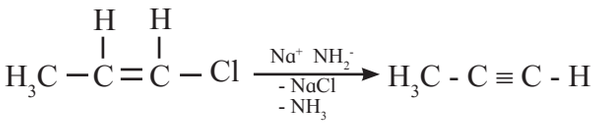
1,2-Dibromoethane



Bromoethene Ethyne



1,2-Dichloropropane



1-Chloropropene Propyne

Can you tell?

Why sodamide is used in second step to remove HX from alkenyl halide in place of alcoholic KOH?

2. From terminal alkynes : Terminal alkynes are the compounds in which hydrogen atom is directly attached to triply bonded carbon atom.

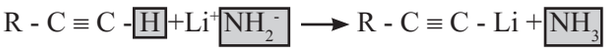
$$H - C \equiv C - H$$

$$R - C \equiv C - H$$

Such hydrogen atom shows appreciable acidity and can be given away as proton on reaction with sufficiently strong base.

In this method a smaller terminal alkyne first reacts with a very strong base like lithium amide to form metal acetylide (Lithium amide is easier to handle than sodamide).

Higher alkynes are obtained by reacting metal acetylides (alkyn-1-yl lithium) with primary alkyl halides.



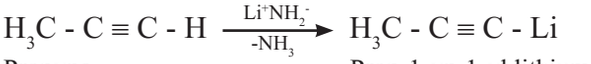
Terminal alkyne Lithium amide Alkyn-1-yl lithium

Alkyn-1-yl lithium Primary alkyl halide Higher alkyne

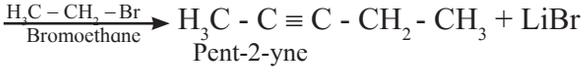
Ethyne Ethynyllithium

$$H - C \equiv C - CH_2 - CH_3 + LiBr$$

But-1-yne



Propyne Prop-1-yn-1-yl lithium



Pent-2-yne

Use your brain power

Convert : 1-Bromobutane to Hex-1yne.

15.3.3 Physical properties of alkynes : The physical propeties of alkynes are similar to those of alkanes and alkenes. They are less dense than water. They are insoluble in water and quite soluble in less polar organic solvents like ether, benzene, carbon tetrachloride. The melting points and boiling points of alkynes increase with an increase in molecular mass (Table 15.5).

Table 15.5 : Melting point and Boiling point of alkynes

Fornula	Name	Molecular mass/u	Physical State	b.p.(K)	m.p.(K)
CH =CH	Ethyne	26	Gas	198	191
$CH = CCH_3$	Propyne	40	Gas	250	171.5
$CH = CCH_2CH_3$	But-1-yne	54	Gas	282	151
$CH = C(CH_2)_2CH_3$	Pent-1-yne	68	Liquid	313	175
$CH = C(CH_2)_3CH_3$	Hex-1-yne	82	Liquid	345	149

15.3.4 Chemical properties of alkynes :

1. Acidity of alkynes :

The hydrogen bonded to C ≡ C triple bond has acidic character. Lithium amide ($LiNH_2$) is very strong base and it reacts with terminal alkynes to form lithium acetylides with the liberation of hydrogen indicating acidic nature of terminal alkynes. Why is it so ? In terminal alkynes, hydrogen atom is directly attached to *sp* hybridized carbon atom. In *sp* hybrid orbital, the percentage of s- character is 50%. An electron in s-orbital is very close to the nucleus and is held tightly. The sp hybrid carbon atom in terminal alkynes is more electronegative than the sp^2 carbon in ethene or the sp^3 carbon in ethane. Due to high electronegative character of carbon in terminal alkynes, hydrogen atom can be given away as proton (H^+) to very strong base.

Examples

$$H - C \equiv C - H \xrightarrow[-NH_3]{Li^+NH_2^-} H - C \equiv C - Li$$

Ethyne — Monolithium ethynide

$$\xrightarrow{Li^+NH_2^-} Li - C \equiv C - Li + NH_3$$

Dilithium ethynide

$$H_3C - C \equiv C - H \xrightarrow[-NH_3]{Li^+NH_2^-} H_3C - C \equiv C - Li$$

Prop-1-yne — Lithium propynide

The relative acidity of alkanes, alkenes and alkynes follows the order

$H - C \equiv C - H > H_2C = CH_2 > H_3C - CH_3$

Can you tell?

Alkanes and alkenes do not react with lithium amide. Give reason.

Use your brain power

Arrange following hydrocarbons in the increasing order of acidic character.
propane, propyne, propene.

Do you know ?

Acidic alkynes react with certain heavy metal ions like Ag^+ and Cu^+ and form insoluble acetylides. On addition of acidic alkyne to solution of $AgNO_3$ in alcohol form a precipitate which indicates that the hydrogen atom is attached to triply bonded carbon. This reaction is used to differentiate terminal alkynes and non-terminal alkynes.

2. Addition of dihydrogen (See method of preparation of alkenes from unsaturated hydrocarbons)

3. Addition of halogens

$$-C \equiv C- + X-X \xrightarrow{CCl_4} -\underset{X}{\overset{}{C}}=\underset{X}{\overset{}{C}}-$$

Alkyne ($X_2 = Cl_2, Br_2$) — 1, 2 - Dihaloalkene

$$\xrightarrow{X-X} -\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-$$

1, 1, 2, 2 - Tetrahalokane

Ethyne reacts with bromine in inert solvent such as carbon tetrachloride to give tetrabromoethane.

$$H - C \equiv C - H + Br - Br \xrightarrow{CCl_4}$$

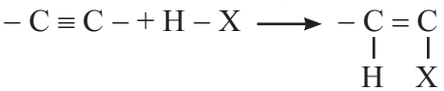
Ethyne — Bromine

$$H-\underset{Br}{\overset{}{C}}=\underset{Br}{\overset{}{C}}-H \xrightarrow{Br-Br} H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H$$

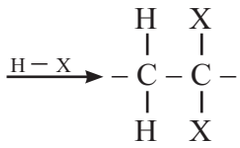
1,2-Bibromoethene — 1,1,2,2-Tetrabromoethane

Red-brown colour of solution of bromine in carbon tetrachloride disappears. This test can be used to detect the presence of unsaturation in given compound.

4. Addition of hydrogen halides

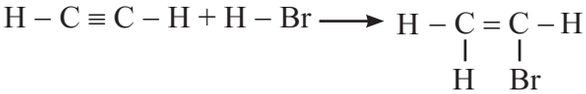


Alkyne (HX = HCl , HBr,HI)

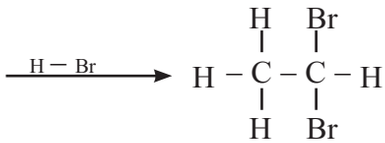


Geminal dihalides

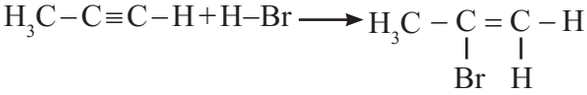
Hydrogen halides (HCl, HBr and HI) add to alkynes across carbon-carbon triple bond in two steps to form geminal dihalides (in which two halogen atoms are attached to the same carbon atom).The addition of HX in both the steps takes place according to **Markovnikov's rule**.



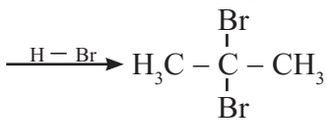
Ethyne Hydrogen bromide 1-Bromoethene



1,1-Dibromoethane50%



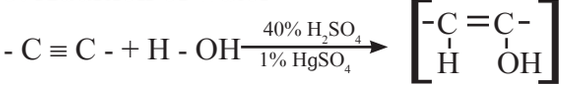
Propyne Hydrogen bromide 2-Bromopropene



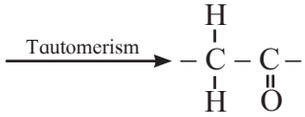
2,2-Dibromopropane

The order of reactivity of hydrogen halides is HI > HBr > HCl

5. Addition of water

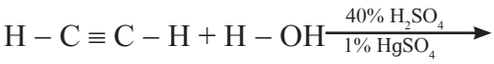


Alkyne Unstable

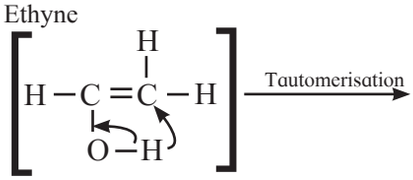


Carbonyl compound

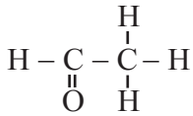
Alkynes react with water in presence of 40% sulphuric acid and 1% mercuric sulphate to form aldehydes or ketones i.e. carbonyl compounds.



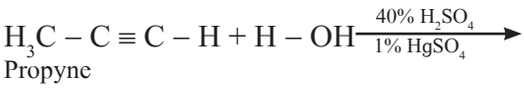
Ethyne



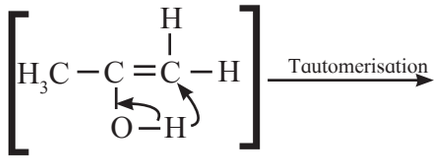
Vinyl alcohol

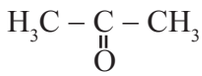


Ethanal



Propyne





Propanone

Use your brain power

Convert : 3-Methylbut-1-yne into 3-Methylbutan-2-one.

15.3.5 Uses of acetylene :

1. Ethyne (acetylene) is used in preparation of Ethanal (acetaldehyde), Propanone (acetone), ethanoic acid (acetic acid).
2. It is used in the manufacture of polymers, synthetic rubber, synthetic fibre, plastic etc.
3. For artificial ripening of fruits.
4. In oxy-acetylene (mixture of oxygen and acetylene) flame for welding and cutting of metals.

15.4 Aromatic Hydrocarbons :

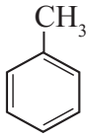
Can you recall?

- What are aromatic hydrocarbons?
- What are benzenoid and non-benzenoid aromatics ?

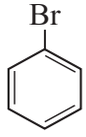
Many organic compounds obtained from natural sources like resins, balsams, oil of wintergreen, etc. possessing pleasant fragrance (aroma = smell) are named as aromatic compounds. Aromatic hydrocarbons (also called arenes) contain only carbon and hydrogen. Benzene is the simplest aromatic compound.

Benzene and all compounds that have structures and chemical properties resembling benzene are classified as aromatic compounds. Examples are :

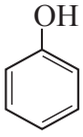
(Benzene)



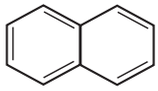
(Methylbenzene)



(Bromobenzene)



(Phenol)



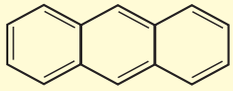
(Naphthalene)

15.4.1 Benzene : The molecular formula of benzene is C_6H_6. Benzene is parent compound of most of the aromatic compounds.

Coal-tar and petroleum are the two large-scale sources of benzene (and aromatic compounds like toulene , phenol, naphthalene.).

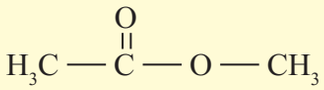
Remember

1. Aromatic compounds contain planar cyclic rings.
2. Not all compounds those resemble benzene have pleasant odour (smell).

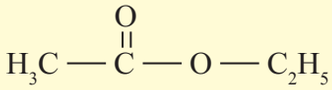


Anthracene is odourless.

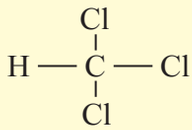
3. Many compounds having pleasant odour do not resemble benzene.



(Methyl acetate)



(Ethyl acetate)



(Trichloromethane or chloroform)

It is a colourless liquid having characteristic odour. Its boiling point is 353K.

It was synthesized by Berthelot (1870) from acetylene. Benzene was originally called **phene** and hence C_6H_5 is called **phenyl group**.

Table 15.6 : Difference between aromatic and aliphatic compounds

Aromatic compounds	Aliphatic compounds
1. Aromatic compounds contain higher percentage of carbon.	1. Aliphatic compounds contain lower percentage of carbon.
2. They burn with sooty flame.	2. They burn with non-sooty flame.
3. They are cyclic compounds with alternate single and double bonds.	3. They are open chain compounds.
4. They are not attacked by normal oxidizing and reducing agents.	4. They are easily attacked by oxidizing and reducing agents.
5. They do not undergo addition reactions easily. They do not decolourise dilute alkaline aqueous $KMnO_4$ and Br_2 in CCl_4, though double bonds appear in their structure.	5. Unsaturated aliphatic compounds undergo addition reactions easily.They decolourise dilute aqueous alkaline $KMnO_4$ and Br_2 in CCl_4.
6. They prefer substitution reactions.	6. The saturated aliphatic compounds give substitution reactions.

15.4.2 Structure of benzene :

1. Molcular formula of benzene, C_6H_6, indicates the high degree of unsaturation.

2. Open chain structure NOT possible : Open chain or cyclic structure having double and triple bonds can be written for C_6H_6. But benzene does not behave like alkenes or alkynes (see Table 15.7). This indicates that benzene can not have the open chain structure.

Table 15.7 : Comparative reactivity of alkenes and benzene

Reaction	Alkene	Benzene
With dil. alka. $KMnO_4$	Decolourisation of purple colour of $KMnO_4$	No decolourisation
With Br_2 in CCl_4	Decolourisation of red brown colour of bromine	No decolourisation
With H_2O in acidic medium	Addition of H_2O molecule	No reaction

3. Evidence of cyclic structure : Benzene yields only one and no isomeric monosubstituted bromobenzene (C_6H_5Br) when treated with equimolar bromine in $FeBr_3$. This indicates that all the six hydrogen atoms in benzene are identical.

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$

This is possible only if benzene has cyclic structure of six carbons bound to one hydrogen atom each.

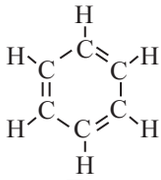
Benzene on catalytic hydrogenation gives cyclohexane.

$$\underset{\text{(Benzene)}}{C_6H_6} + 3H_2 \xrightarrow[\Delta]{Ni} \underset{\text{(Cyclohexane)}}{C_6H_{12}}$$

This confirms the cyclic structure of benzene and three C = C in it.

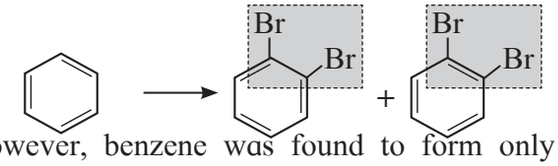
4. Kekulé structure of benzene :

August Kekulé in 1865 suggested the structure for benzene having a cyclic planar ring of six carbon atoms with alternate single and double bonds and hydrogen atom attached to each carbon atom.



Usually written as

The Kekulé structure indicates the possibility of two isomeric 1,2-dibromobenzenes. In one of the isomers, the bromine atoms would be attached to the doubly bonded carbon atoms whereas in the other, they would be attached to single bonded carbons.

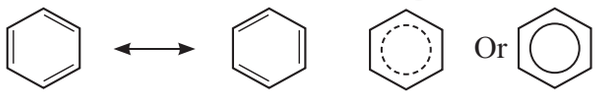


However, benzene was found to form only one ortho-disubstituted benzene. This problem was overcome by Kekule' by suggesting the concept of oscillating nature of double bonds in benzene as given below.

Even with this modification, Kekule' structure of benzene failed to explain unusual stability and preference to substitution reactions rather than addition reactions, which was later explained by resonance.

5. Stability of benzene:

Benzene is a hybrid of various resonance srtuctures.The two structures, A and B given by Kekulé are the main contributing structures. The resonance hybrid is represented by inserting a circle or a dotted circle inscribed in the hexagon as shown in (C). The circle represents six electrons delocalized over the six carbon atoms of benzene ring.



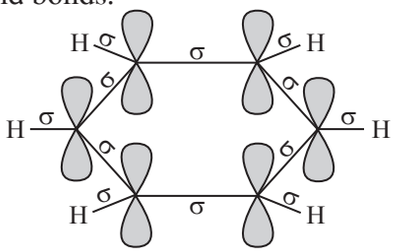
(A) (B) (C)

A double headed arrow between the resonance structures is used to represent the resonance phenomenon.

Stability of benzene : The actual molecule is more stable than any of its resonance structures. For benzene, the stability due to resonance

is so high that π-bonds of the molecule resist breaking. This explains lack of reactivity of benzene towards addition.

The orbital overlap gives us better picture of structure of benzene. All six carbon atoms in benzene are sp^2 hybridised. Two sp^2 hybrid orbitals of carbons overlap and form carbon-carbon sigma (σ) bond and the remaining third sp^2 hybrid orbital of each carbon overlaps with s orbital of a hydrogen atom to form six C-H sigma bonds.



The unhybrid p orbitals of carbon atoms overlap laterally forming π bonds. There are two possibilities of forming three π bonds by overlap of p orbitals of C_1-C_2, C_3-C_4, C_5-C_6 or C_2-C_3, C_4-C_5, C_6-C_1, respectively, as shown in Fig. 15.5; both are equally probable. According to **resonance theory** (Chapter 5) these are two resonance structures of benzene.

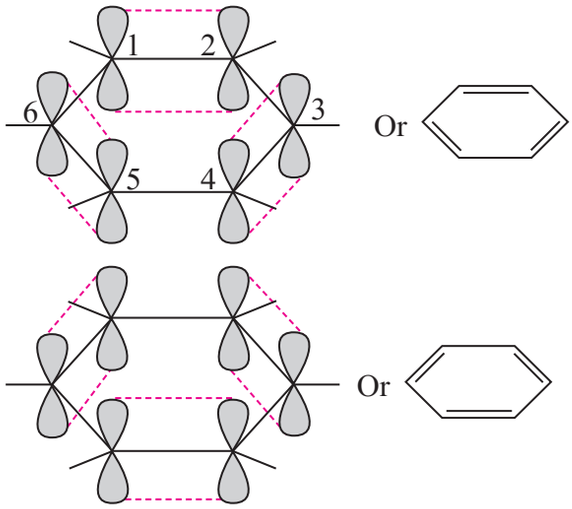


Fig. 15.5 Overlap of p orbitals in benzene

According to **molecular orbital (MO) theory** (Chapter 5) the six p orbitals of six carbons give rise to six molecular orbitals of benzene. Shape of the most stable MO is as shown in Fig. 15.6.

Three of these π molecular orbitals lie above and the other below those of free carbon atom energies.

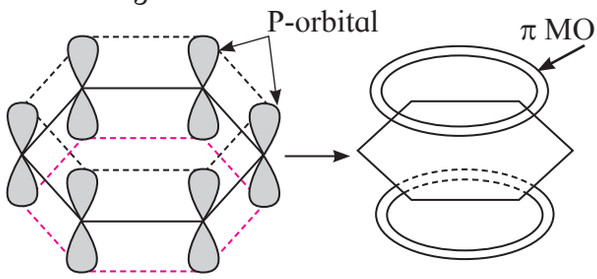
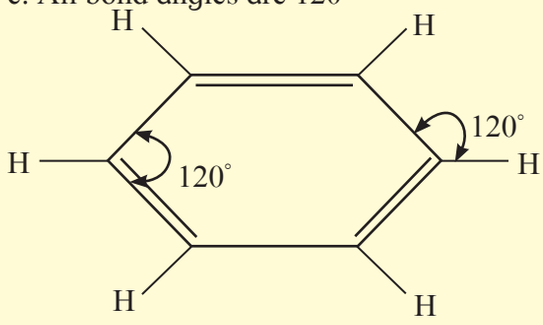


Fig 15.6 : Representative π molecular orbital in benzene

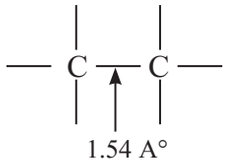
Remember

In benzene , a. All carbon and hydrogen atoms lie in the same plane.
b. Six sigma (σ) bonds lie in the same plane.
c. All bond angles are 120^0

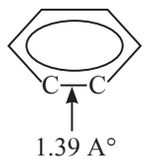


The six electrons of the p orbitals cover all the six carbon atoms and are said to be delocalized. Delocalization of π electrons results in stablity of benzene molecule.

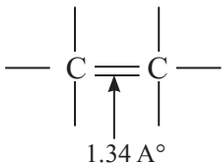
6. Bond parameters of benzene : X-ray diffraction data indicate that all C-C bond lengths in benzene are equal (139 pm) which is an intermediate between C-C (154 pm) and C=C bond (133pm). Thus absence of pure double bond in benzene accounts for its reluctance to addition reactions under normal conditions, which explains unusual behaviour of benzene (Refer to sec.14.6.5).



Single-bond lenght



Benzene-bond length



Double-bond length

15.4.3 Aromatic character (Huckel Rule) :

Benzene undergoes substitution reaction rather than addition reactions. This property is common to all aromatic compounds and is referred to as **aromaticity** or **aromatic character**. The aromatic character of benzene is correlated to its structure.

Aromaticity is due to extensive cyclic delocalization of p electrons in planar ring structures.

The following **three rules of aromaticity** are useful in predicting whether a particular compound is

aromatic or non-aromatic.

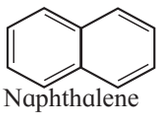
1. Aromatic compounds are cyclic and planar (all atoms in ring are sp^2 hybridized).

2. Each atom in aromatic ring has a p-orbital. The p-orbitals must be parallel so that continuous overlap is possible around the ring.

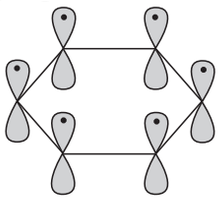
3. Huckel Rule : The cyclic π molecular orbital formed by overlap of p-orbitals must contain (4n + 2) p electrons, where n= integer 0,1,2,3 ...etc.

Let us apply these rules to the following compounds


Benzene


Naphthalene

1. Benzene : It is cyclic and planar. It has three double bonds and six π electrons. It has a p orbital on each carbon of the hexagonal ring. Hence a continuous overlap above and below the ring is posssible.



This compound is aromatic, 4n + 2 = Number of π electrons.

4n + 2 = 6, $\therefore$ 4n = 6-2 =4

n = 4/4 = 1, Here 'n' comes out to be an integer. Hence benzene is aromatic.

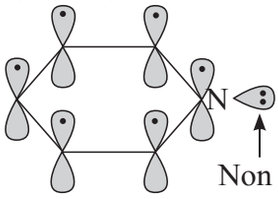
2. Naphthalene : It is cyclic and planar. It has 5 double bonds and 10 π electrons.It has p orbital on each carbon atom of the ring. Hence a continuous overlap around the ring is posssible. This is in accordance with Huckel rule.

4n + 2 = Number of π electrons

4n + 2 = 10, $\therefore$ 4n = 10 -2 = 8

n = 8/4 = 2, Here 'n' comes out to be an integer. Hence napthalene is aromatic.

3. Pyridine : Pyridine has three double bonds and 6 π electrons. The six p orbital containing six electrons form delocalized p molecular orbital. The unused sp^2 hybrid orbital of nitrogen containing two non-bonding electrons is as it is.

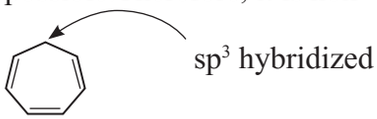


4n + 2 = Number of p electrons

4n + 2 = 6, $\therefore$ 4n = 6 -2 = 4

n = 4/4 = 1, Here 'n' comes out to be an integer. Hence pyridine is aromatic.

4. Cycloheptatriene : It is cyclic and planar. It has three double bonds and 6 π electrons. But one of the carbons is saturated (sp^3 hybridized) and does not possess a p orbital. Hence a continuous overlap around the ring is not possible.Therefore, it is non- aromatic.



15.4.4 Preparation of aromatic compounds

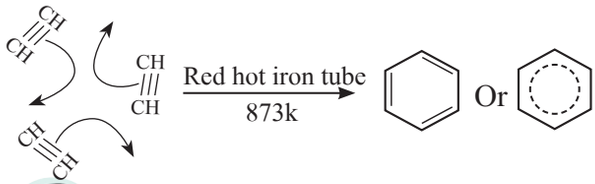
a. Industrial source of aromatic compounds

Coal tar and petroleum are major sources of aromatic compounds.

b. Methods of preparation of benzene

1. From ethyne (By trimerization) : Alkynes when passed through a red hot iron tube at 873 K, polymerize to form aromatic hydrocarbons.

Ethyne when passed through a red hot iron tube at 873 K undergoes trimerization to form benzene.

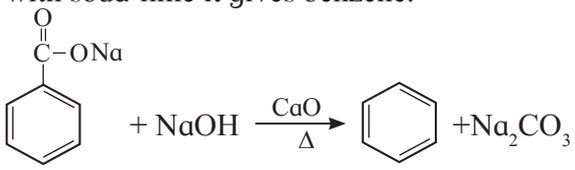


Can you recall?

What is decarboxylation ?

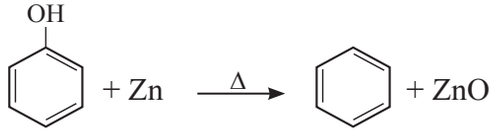
2.From sodium benzoate :
(By decarboxylation)

When anhydrous sodium benzoate is heated with soda-lime it gives benzene.



Sodium benzoate — Benzene

3. From phenol (By reduction) : When vapours of phenol are passed over heated zinc dust, it gives benzene.



Phenol — Benzene

15.4.5 Physical properties of benzene

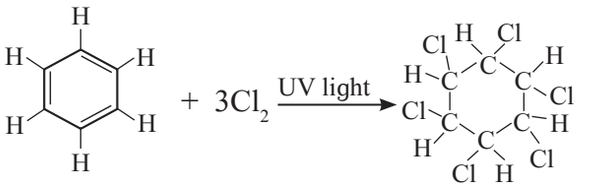
1. Benzene is colourless liquid.
2. Its boiling point is 353K and melting point is 278.5 K.
3. It is isoluble in water. It forms upper layer when mixed with water.
4. It is soluble in alcohol, ether, and chloroform.
5. Benzene vapours are highly toxic which on inhalation lead to unconsciousness.

15.4.6 Chemical properties of benzene

Aromatic compounds are characterised by electrophilic substitution reactions. However, they undergo addition and oxidation reactions under special conditions. Some reactions of benzene are discussed below.

I. Addition reactions

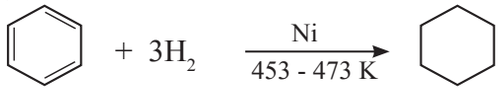
i. Addition of chlorine : Benzene when treated with chlorine in presence of bright sunlight or UV light, adds up three molecules of chlorine to give benzene hexachloride .



Benzene — Benzene hexachloride (BHC)

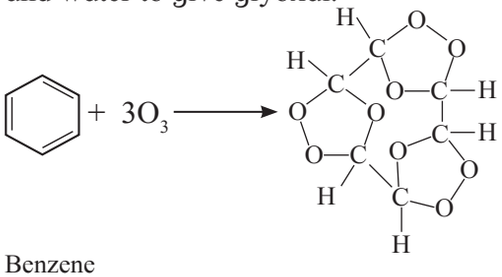
γ - isomer of benzene hexachloride is called **gammexane** or **lindane** which is used as insecticide.

ii. Addition of hydrogen : When a mixture of benzene and hydrogen gas is passed over heated catalyst nickel at 453 K to 473 K,cylohexane is formed.

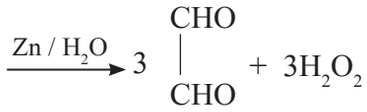


Benzene (C_6H_6) — Cyclohexane (C_6H_{12})

iii. Addition of ozone : When benzene is treated with ozone in presence of an inert solvent carbon tetrachloride, benzene triozonide is formed which is then decomposed by zinc dust and water to give glyoxal.



Benzene

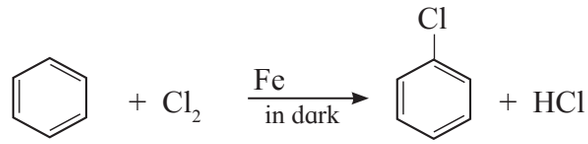


Ethanedial or glyoxal

II. Substitution reactions : Benzene shows electrophilic substitution reactions, in which one or more hydrogen atoms of benzene ring are replaced by **electrophilic groups** like -Cl, -Br, $-NO_2$, $-SO_3H$, -R (alkyl group) , -COR (Acyl group) etc. (see Chapter 14).

i. Halogenation : In this reaction, hydrogen atom of benzene ring is replaced by halogen atom .

Chlorination



Benzene Chlorobenzene

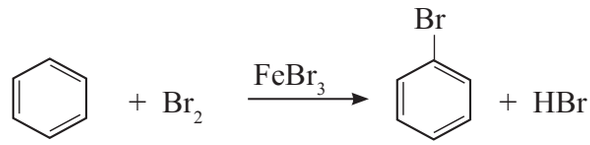
Chlorine reacts with benzene in dark in the presence of iron or ferric chloride or anhydous aluminium chloride or red phosphorous as catalyst to give chlorobenze .

Electrophile : $Cl^{\oplus}$, Chloronium ion

Formation of the electrophile :

$Cl - Cl + FeCl_3 \longrightarrow Cl^{\oplus} + [FeCl_4]^{\ominus}$

Bromination of benzene is similar to chlorination :



Benzene Bromobenzene

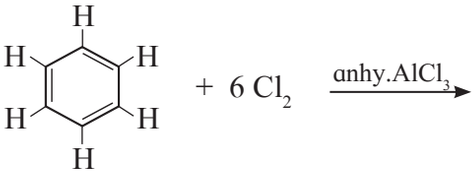
Electrophile : $Br^{\oplus}$,

Formation of electrophile :

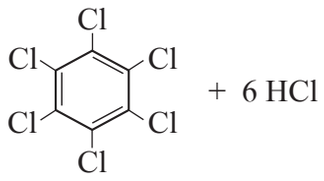
$Br - Br + FeBr_3 \longrightarrow Br^{\oplus} + [FeBr_4]^{\ominus}$

Iodination of benzene is **not possible** as it is reversible process.

With excess of chlorine, benzene gives hexachlorobenzene.

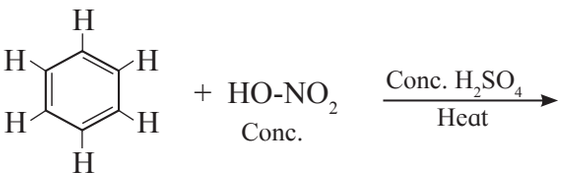


Benzene

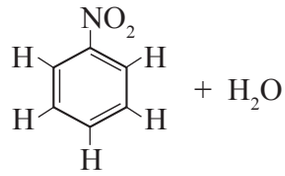


Hexachlorobenzene

ii. Nitration :



Benzene



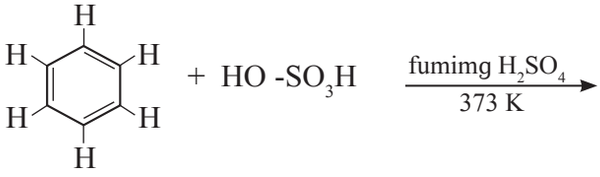
Nitrobenzene

When benzene is heated with a mixture of concentrated nitric acid and concentrated sulfuric acid (nitrating mixture) at about 313 K to 333 K , it gives nitrobenzene.

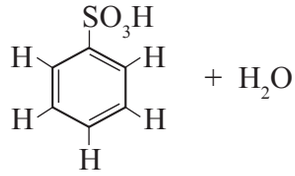
Electrophile : $NO_2^{\oplus}$, nitronium ion.

Formation of the electrophile : $HO - NO_2 + 2H_2SO_4 \rightleftharpoons 2HSO_4^{\ominus} + H_3O^{\oplus} + NO_2^{\oplus}$

iii. Sulfonation :



Benzene



Benzenesulfonic acid

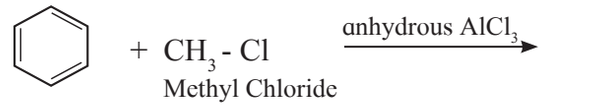
When benzene is heated with fuming sulfuric acid (oleum) at 373 K, it gives benzene sulfonic acid.

Electrophile : SO_3 , free sulfur trioxide

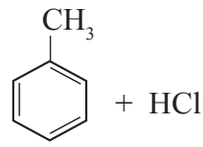
Formation of the electrophile :

$2H_2SO_4 \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus} + SO_3$

iv. Friedel-Craft's alkylation reaction :



Benzene



Methylbenzene
(Toluene)

When benzene is treated with an alkyl halide like methyl chloride in the presence of anhydrous aluminium chloride, it gives toluene.

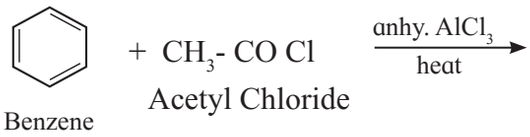
The reaction is used to extend the chain outside the benzene ring.

Electrophile : $R^{\oplus}$

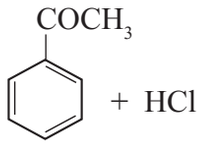
Formation of the electrophile :

$R - Cl + AlCl_3 \longrightarrow R^{\oplus} + AlCl_4^{\ominus}$

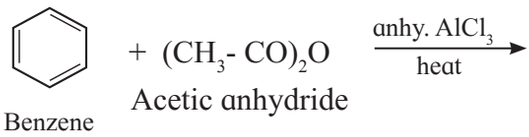
v. Friedel-Craft's acylation reaction :



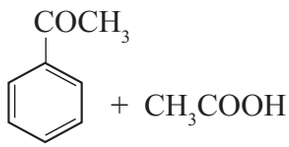
Benzene Acetyl Chloride



1- Phenylethanone or Acetophenone



Benzene Acetic anhydride



1- Phenylethanone or Acetophenone

When benzene is heated with an acyl halide or acid anhydride in the presence of anhydrous aluminium chloride, it gives corresponding acyl benzene.

Electrophile : $R\text{-}C^{\oplus}{=}O$ acylium ion

Formation of the electrophile : $R - COCl + AlCl_3 \longrightarrow R\text{-}C^{\oplus}{=}O + AlCl_4^{\ominus}$

6. Combustion : When benzene is heated in air , it burns with sooty flame forming carbon dioxide and water.

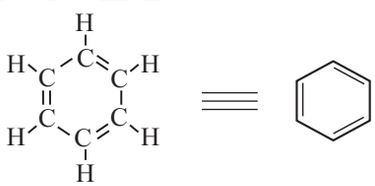
$C_6H_6 + 15/2\ O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$

General combustion reaction for any hydrocarbon (C_xH_y) can be represented as follows:

$C_xH_y + (x + y/4)\ O_2 \longrightarrow x\ CO_2 + y/2\ H_2O$

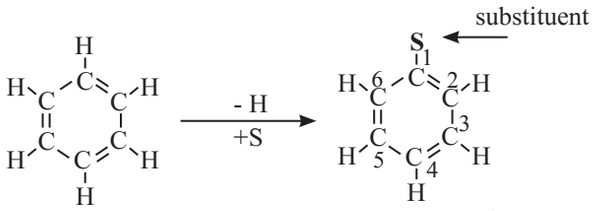
15.4.7 Directive influence of a functional group in monosubstituted benzene

Structure of benzene :



In benzene, all hydrogen atoms are equivalent. Therefore, only one product is possible when it undergoes electrophilic substitution reactions.

Monosubstituted benzene :



Monosubstituted benzene

Positions of carbon atoms in mono substituted benzene :

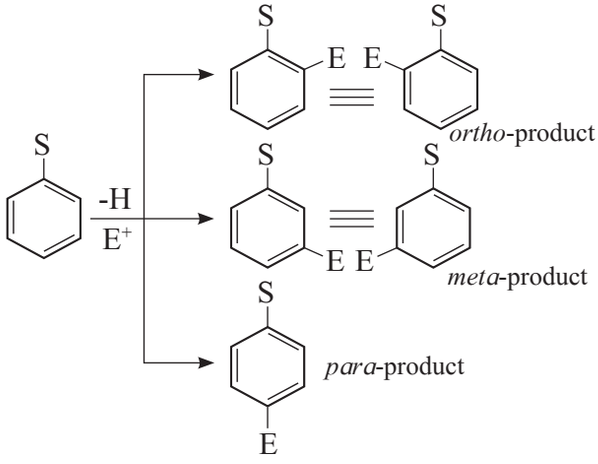
The positions 2 and 6 are equivalent and give ortho (o-) products.

The position 3 and 5 are equivalent and give meta (m-) products.

The position 4 is unique and and gives para (p-) product.

Now in benzene , five positions are available for electrophilic substitution.

When monosubstituted benzene is subjected to further electrophilic substitution, the second substituent i.e. electrophile (see Chapter 14) or incoming group (E) can occupy any of these positions and give three disubstituted products. But these products are not formed in equal amounts.

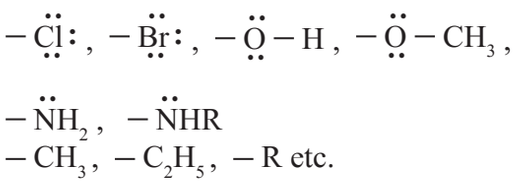


Two types of behaviour are observed.

a. ortho- and para - products or b. meta-products are found as major products :

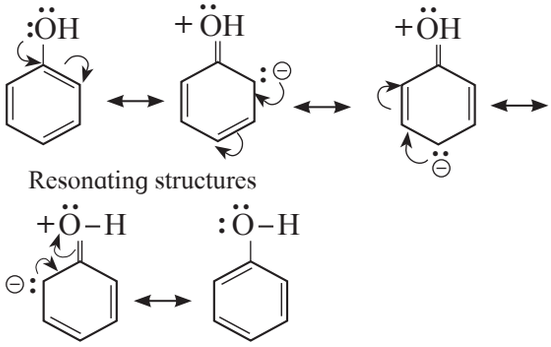
This behaviour mainly depends on the nature of the substituent (S) already present in the benzene ring and not on the nature of second substituent (E) i.e. incoming group.

Ortho and para directing groups :



The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups.

Ortho and para directive influence of -OH group : The resonance theory clearly explains why certain substituents are ortho/para or meta directing. Let us study the various resonance structures of phenol (see Chapter 14).



Resonating structures

It is clear from the above resonance structures that the ortho and para positions have a greater electron density than the meta positions. Therefore, -OH group activates the benzene ring for the attack of second substituent E at these electron -rich centres.

Remember

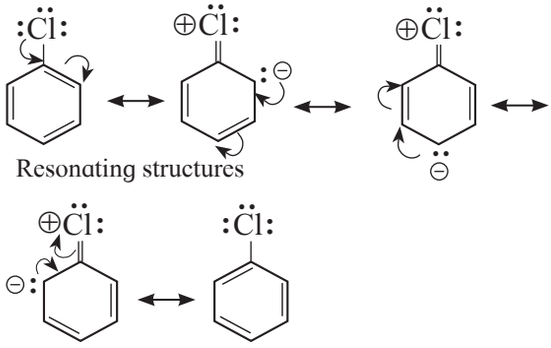
Due to -I effect of -OH group (see Chapter 14), the electron density on ortho positions of the benzene ring gets slightly reduced. Thus resonance effect and inductive effect of OH group act opposite to each other but +R effect of -OH is more powerful than -I effect.

All ortho and para directing groups possess nonbonding electron pair on the atom which is directly attached to aromatic ring.

Methyl group is an exception : The only exception to above rule is methyl or alkyl groups. It is ortho and para directing, although it has no nonbonding electron pair on the key atom.This is explained on the basis of special type of resonance called hyperconjugation or no bond resonance (see Chapter 14).

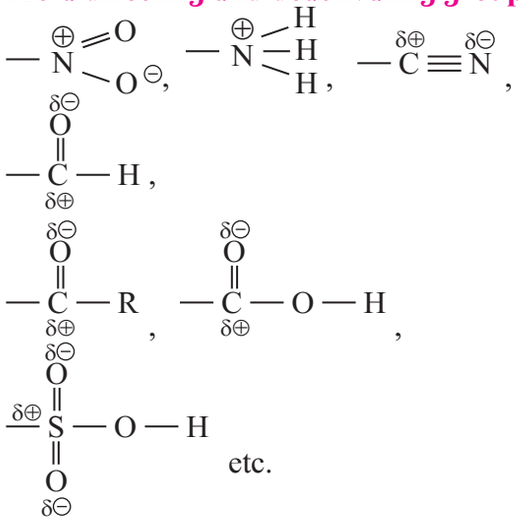
In case of **aryl halides**, halogens are moderately deactivating. Because of their strong -I effect, overall electron density on the benzene ring decreases. It makes the electrophilic substitution difficult. However, due to resonance the electron density on ortho and para positions is greater than meta positions. Halogens are ortho and para directing.

Let us study the various resonanting structures of chlorobenzene.



Resonating structures

Meta directing and deactivating groups

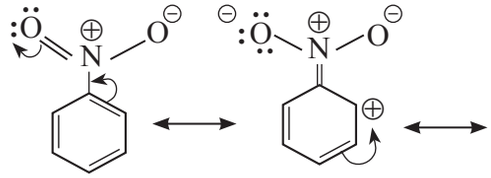


etc.

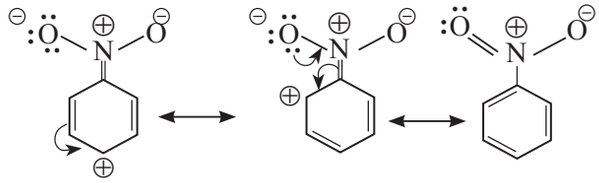
All meta directing groups have positive (or partial positive) charge on the atom which is directly attached to an aromatic ring.

The groups which direct the incoming group to meta positions are called **meta directing groups**.

Metadirective influence of -NO_2 group can be explained by resonance theory : Meta directing group withdraws electrons from the aromatic ring by resonance, making the ring electron-deficient. Therefore, meta groups are ring deactivating groups. Due to -I effect , -NO_2 group reduces electron density in benzne ring on ortho and para positions.So the attack of incoming group becomes difficult at ortho and para positions. Incoming group can attack on meta positions more easily. Let us study the various resonance structures of nitrobenzene.



Resonating structures



It is clear from the above resonance structures that the ortho and para positions have comparatively less electron density than at meta positions. Hence, the incoming group/ electrophile attacks on meta positions.

15.4.8 Carcinogenicity and Toxicity of benzene :

Benzene is both toxic and carcinogenic (cancer causing). In fact, it might be considered "the mother of all carcinogens" as a large number of carcinogens have structures those include benzene rings. Several polycyclic aromatic compounds (containing more than two fused benzene rings) are produced by incomplete combustion of tobacco, coal and petroleum. In liver, benzene is oxidized to an epoxide. Benzopyrene is converted into an epoxy diol. These substances are carcinogenic and can react with DNA which can induce mutation leading to uncontrolled growth of cancer cells.

Internet my friend

1. chemed.chem.purdue.edu>1organic>Organic Chemistry
2. www.ncert.nic.in>ncerts>kech206(pdf)
3. https://www.britannica.com>science>benzene
4. https://pubchem.ncbi.nlm.nih.gov>Benzene

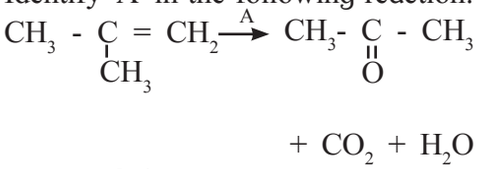
Exercises

1. Choose correct options

A. Which of the following compound has highest boiling point ?
   a. n-pentane
   b. iso-butane
   c. butane
   d. neopentane

B. Acidic hydrogen is present in :
   a. acetylene
   b. ethane
   c. ethylene
   d. dimethyl acetylene

C. Identify 'A' in the following reaction:



   a. $KMnO_4/H^+$
   b. alkaline $KMnO_4$
   c. dil. H_2SO_4/1% $HgSO_4$
   d. $NaOH/H_2O_2$

D. Major product of chlorination of ethyl benzene is :
   a. m-chlorethyl benzene
   b. p - chloroethyl benzene
   c. chlorobenzene
   d. o - chloroethylbenzene

E. 1 - chloropropane on treatment with alc. KOH produces :
   a. propane
   b. propene
   c. propyne
   d. propyl alcohol

2. Name the following :

A. The type of hydrocarbon that is used as lubricant.

B. Alkene used in the manufacture of polythene bags.

C. The hydrocarbon said to possess carcinogenic property.

D. What are the main natural sources of alkane?

E. Arrange the three isomers of alkane with malecular formula C_5H_{12} in increasing order of boiling points and write their IUPAC names.

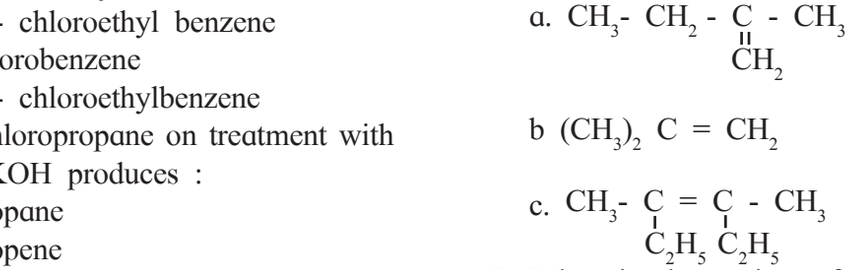
F. Write IUPAC names of the products obtained by the reaction of cold concentrated sulphuric acid followed by water with the following compounds.
   a. propene b. but-l-ene

G. Write the balanced chemical reaction for preparation of ethane from
   a. Ethyl bromide
   b. Ethyl magnesium iodide

H. How many monochlorination products are possible for
   a. 2-methylpropane ?
   b. 2-methylbutane ?
   Draw their structures and write their IUPAC names.

I. Write all the possible products for pyrolysis of butane.

J. Which of the following will exhibit geometical isomerism ?



K. What is the action of following on ethyl iodide ?
   a. alc, KOH
   b. Zn, HCl

L. An alkene 'A' an ozonolysis gives 2 moles of ethanal. Write the structure and IUPAC name of 'A'.

M. Acetone and acetaldehyde are the ozonolysis products of an alkene. Write the structural formula of an alkene and give IUPAC name of it.

N. Write the reaction to convert
   a. propene to nypropylalcohol.
   b. propene to isoproyl alcohol.

O. What is the action of following on but-2-ene ?
   a. dil alkaline $KMnO_4$
   b. acidic $KMnO_4$

P. Complete the following reaction sequence :

$$HC \equiv CH \xrightarrow{LiNH_2} A \xrightarrow{CH_3CH_2Cl} B \xrightarrow{HBr} C$$

Comment on the acidic nature of B.

Q. Write the balanced chemical reactions to get benzene from
   a. Sodium benzoate.
   b. Phenol.

R. Predict the possible products of the following reaction.
   a. chlorination of nitrobenzene,
   b. sulfonation of chlorobenzene,
   c. bromination of phenol,
   d. nitration of toluene.

3. Identify the main product of the reaction

a. $CH_3\text{-}CH_2\text{-}CH_3 \xrightarrow[\Delta]{O_2}$

b. $CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3 \xrightarrow[373K]{60\%\ H_2SO_4}$

c. $HC \equiv C\text{-}CH_3 \xrightarrow[\text{Pd-C/quinoline}]{H_2}$

d. $H\text{-}C\text{-}H + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4}$

4. Read the following reaction and answer the questions given below.

$$CH_3 - \underset{\underset{CH_3}{|}}{C} = CH_2 + HBr \xrightarrow[\text{peroxide}]{\text{benzoyl}} CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2Br$$

a. Write IUPAC name of the product.
b. State the rule that governs formation of this product.

5. Identify A, B, C in the following reaction sequence :

$$CH_3 - CH = CH_2 \xrightarrow[\text{room temperature}]{Br_2/CCl_4} A \xrightarrow{Zn} B \xrightarrow[KMnO_4]{\text{dil. alka.}} C$$

6. Identify giving reason whether the following compounds are aromatic or not.

A. 

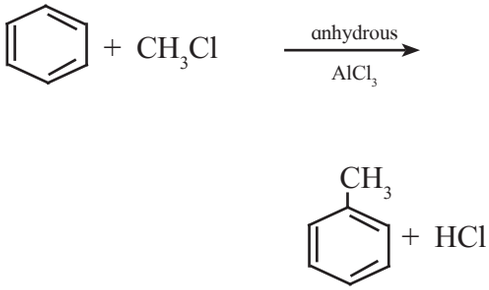
B. 

C. 

D. 

7. Name two reagents used for acylation of benzene.

8. Read the following reaction and answer the questions given below.



A. Write the name of the reaction.
B. Identify the electrophile in it.
C. How is this electrophile generated?

Activity :

Prepare chart of hydrocarbons and note down the characteristics.

16. Chemistry in Everyday Life

Can you recall?

1. What are the components of balanced diet ?
2. Why is food cooked ? what is the difference in the physical states of uncooked and cooked food?
3. What are the chemicals that we come across in everyday life ?

The life, the atmosphere, the earth and the universe, all have evolved over billions of years to the present state. The evolution continues progress and accompanied by a variety of chemical changes. Natural phenomena such as weathering, lightening, irruption of volcanoes, photosynthesis, ripening of fruit, fermentation, release of fragrance by blooming flowers and many others take around us involve intricate chemistry. Chemistry is involved in a variety of life processes those occur within and across our body. Human civilization in different regions of the world discovered uses of various plant, animal and mineral products for benefits of human life. With the advent of modern science, scientist discovered structures of various constituent chemicals in natural materials. Synthetic organic chemistry has led to advancement in science. Synthesis of natural molecules and new molecules with structural variation revolutionalized materials are used in all the walks of human life. This influence is seen in all aspects of the basic needs, such as food, clothing, shelter and beyond.

In this chapter, we consider some aspects of **food chemistry**, **medicinal chemistry** and **chemistry of cleansing materials** with reference to compounds having simple structural features.

16.1 Basics of food chemistry

Food provides **nutrients** these are used by the body as the source of energy. These nutrients also regulate growth, maintain and repair body tissues. The nutrients comprise carbohydrates, lipids, proteins, vitamins, minerals and water. Grains, fruits and vegetables provide carbohydrates and vitamins; meat, fish, eggs, dairy products and pulses provide proteins and vitamins. Lipids are provided by vegetable oils, dairy products and animal fats.

Most nutrients are organic macromolecules. **Proteins** and **carbohydrates** are **polymeric** materials. As a result of food **digestion,** the polymeric proteins and carbohydrates ultimately break down into monomers, namely, α- **amino acids** and **glucose,** respectively, under the influence of **enzymes**. Cooking makes food easy to digest. During the cooking process, high polymers of carbohydrates or proteins are hydrolysed to smaller polymers. The uncooked food mixture, described as heterogeneous suspension, becomes a colloidal matter on cooking. Because of smaller size of the resulting constituent nutrient molecules, **cooked food** is easier to digest than the uncooked food.

16.1.2 Food quality chemistry :

Just think

1. Why is food stored for a long time ?
2. What methods are used for preservation of food ?
3. What is meant by quality of food ?

Quality of food is an important aspect of food chemistry. Food quality is described in terms of parameters such as flavour, smell, texture, colour and microbial spoilage. Enzymes are present naturally in all foods.

Quality of foods changes on shelving mostly due to enzyme action, chemical reactions with the environment and the action of microorganisms. Some of these effects are beneficial. For example, setting of milk into curd and raising flour dough to make bread is brought about by deliberate action of microorganisms. Most changes brought about by microorganisms and interaction with the environment however, adversely affect the food quality.

Problem 16.1

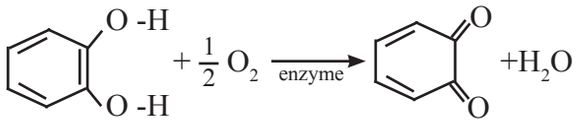
How are the chemical reactions of food stuff with the environment controlled during storage ?

Solution :

Primarily the oxygen and microorganisms in air are responsible for adverse effects on stored food. The exposure of stored food to atmosphere is minimized by storing them in air tight container, evacuation or filling the container with N_2 gas. Rate of a chemical reaction decreases with the lowering of temperature. Thus refregeration is useful for controlling chemical reaction of food stuff with envrionment. The reactions of food stuff with environment are catalyzed by enzymes. Due to boiling, the enzymes become denatured and the reactions are controlled.

Food preservation and food processing methods aim at prevention of undesirable changes and attempt about desirable changes in food. The following cases illustrate some aspects of food quality and the underlying chemisty.

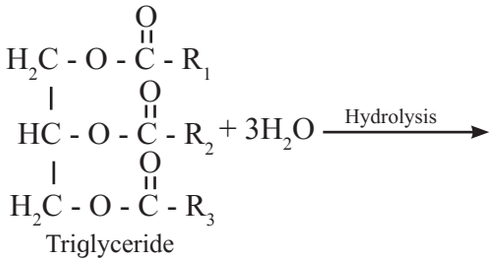
i. Browning of cut fruit/vegetables : When fruits such as banana, apple or vegetables such as potato, bottelgourd are peeled and sliced, sooner or later they turn brown. Cutting action damage the cells resulting in release of chemicals. With the pH prevailing in fruit/ vegetables, the polyphenols released are oxidised with oxygen in air owing to action from an enzyme to form quinones.



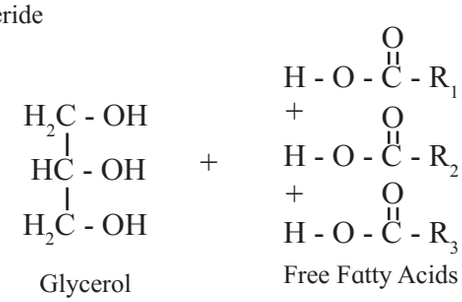
a poly phenol a quinone

Quinones undergo further reactions including polymerization giving brown coloured products named **tannins**. This browning reaction can be slowed down using reducing agents such as SO_2, ascorbic acid (vitamin C) or by change of pH by adding edible acid such as lemon juice (citric acid) or vinegar.

ii. Rancidity of oils and fats : On keeping for long time, oils and fats develop an unpleasant or **rancid** smell and disagreeable taste. Fats are triesters of fatty acids (long chain carboxylic acids) and glycerol (propane - 1, 2, 3 - triol). One cause of rancidity is release of fatty acids produced during hydrolysis of fats brought about by water present in food.



Triglyceride



Glycerol Free Fatty Acids

The hydrolysis of fats occurs rapidly in the presence of certain microorganisms and is an enzyme catalysed reaction. Rancidity of milk and butter is due to the release of four, six and eight carbon fatty acids (butanoic, hexanoic and octanoic acids) on hydrolysis. Chocolate develops oily or fatty flavour due to release of palmitic, stearic and oleic acids on hydrolysis. Lauric acid on hydrolysis gives a soapy flavour to coconut oil.

The second cause of rancidity of oils and fats is **oxidation** by molecular oxygen in the air. Many vegetable oils have one or more C=C double bonds in the fatty acid part of their structure. These are called mono or poly unsaturated fats. The unsaturated fat molecules break down during the oxidation and form **volatile aldehydes** and **carboxylic acids** which give the unpleasent rancid taste.This is called **oxidative rancidity.** It is caused by **free radical** reaction initiated by light (photo oxidation) or catalysed by either enzymes or metal ions. Polyunsaturated oils containing greater number of C=C double bonds and usually become rancid very quickly. High temperature increases the rate of air oxidation of unsaturated fats. Extensive oxidation can lead to some **polymerization** with consequent increase in viscosity and browning.

iii. Saturated, unsaturated and trans fats :

Can you recall?

1. How is Vanaspati Ghee made ?
2. What are the physical states of peanut oil, butter, animal fat, vanaspati ghee at room temperature ?

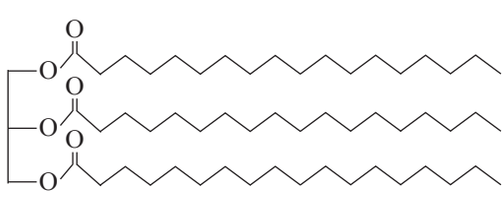
You have noted earlier that fats are triglycerides of fatty acids. Animal fats mostly contain saturated fatty acids, while vegetable oils contain unsaturated fatty acids as well. Long chains of tetrahedral carbon atoms in a saturated fatty acid get packed closely together. Moreover, van der Waal's forces between the long saturated chains are sufficiently strong to convert saturated fats into solid form at room temperature.

The long carbon chains of unsaturated fatty acids contain one or more C=C double bonds. This produces one or more '**kinks**' in the chain, (see the Fig. 16.1) which prevent the molecules from packing closely together. The van der Waals forces between the unsaturated chains are weak. The melting points of unsaturated fats therefore, are lower.

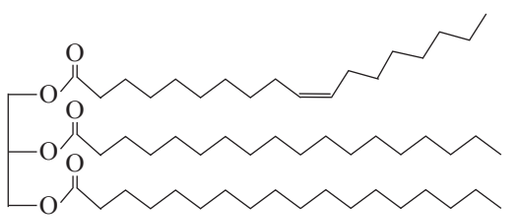
Natural fats are mixtures of triglycerides. They do not have sharp melting points, and usually melt over a range of temperatures. The more unsaturated the fat lower is its melting point and less crystalline it is. Some examples of fats are given in Table 16.1.

A C=C can have geometrical isomers **cis and trans**. In the **cis** form of an unsaturated fatty acid the two hydrogens on the two double bonded carbons are on the same side of the double bond, whereas they are on the opposite sides in the **trans** isomer. The **cis** isomer is the most common form of unsaturated fats. The **trans** form occurs only in animal fats and processed unsaturated fats. **Trans fats** are **difficult to metabolize** and may build up to dangerous levels in fatty tissue.

Fats in the form of **lipoprotein** are used in the body for transport of cholesterol. Excessive low density lipoprotein **(LDL)** results in deposition of **cholesterol in blood vessels**, which in turn, results in the increased risk of cardio vascular disease. There is some evidence that eating large amounts of saturated or trans unsaturated fats, increase the tendency of cholesterol getting deposited in blood vessels. Cis fats do not cause formation of such deposits and decrease chance of developing coronary heart disease.



a. A saturated fat molecule



b. An unsaturated fat molecule.

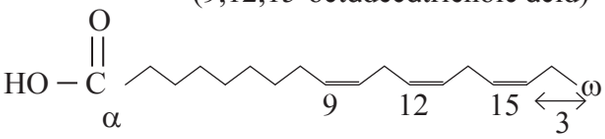
Fig. 16.1 Molecular shapes of fats (A schematic representation)

Table 16.1 : Natural fats and their physical states

Mainly Saturated fats	Mainly mono-unsaturated fats	Mainly poly-unsaturated fats
Coconut fat/oil, butter fat, lard, margarine, vanaspati ghee	Olive oil, peanut oil, canola oil	Safflower oil, sunflower oil, soyabean oil, corn oil, fish oil
solid	liquid	liquid

iv. Omega-3 : Two categories of the natural unsaturated fats of concern include those containing either Omega-3 or Omega-6 fatty acids. These names are given for the position of the double bond in a long carbon chain of the fatty acid. Omega denotes the last carbon of the carbon chain. Omega-3 fatty acids have C=C bond between the third and fourth carbon from the end of a carbon chain.

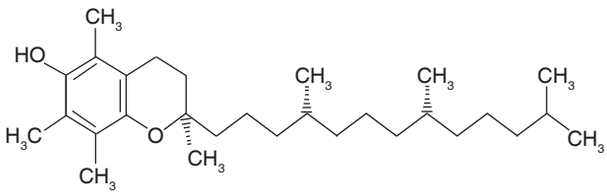
For example : Linolenic Acid (9,12,15-octadecatrienoic acid)



Omega-3 fats are found to raise the High density lipoprotein HDL (good cholesterol) level of blood. On the contrary, Omega-6 fats are considered to have risk of high blood pressure. Foods such as walnuts, flaxseeds, chia seeds, soyabeans, cod liver oil are rich source of Omega- 3 fatty acids.

v. Antioxidants as food additives : An antioxidant is a substance that delays the onset of oxidation or slows down the rate of oxidation of food stuff. It is used to extend the shelf life of food. Antioxidants react with oxygen-containg free radicals and thereby prevent oxidative rancidity.

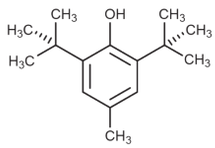
For example, vitamin E (tocopherol) is



Vitamin E (Tocopherol)

a very effective natural antioxidant which is added to pack edible oils. The phenolic OH group in its structure is responsible for its antioxidant activity, while the long chain of saturated carbons makes it fat soluble. It is found in foods such as wheat germ, nuts, seeds, green leafy vegetables and oils like safflower oil.

For economic reason **synthetic antioxidants** are used as additives to increase the shelf-life of packed foods. Common structural units found in synthetic antioxidants are phenolic OH group and tertiary butyl group. For example BHT, which is 3, 5-di-tert-butyl-4-hydroxytoluene.



BHT

16.2 Compounds with medicinal properties

Can you tell?

1. What type of medicine is applied to a bruise ?
2. When is an antipyretic drug used ?
3. What is meant by a broad spectrum antibiotic ?
4. What is the active principle of cinnamon bark ?

A chemical which interacts with biomolecules such as carbohydrates, lipids, proteins and nucleic acid and produces a biological response is called **drug**. A drug having therapeutic and useful biological response is used as **medicine**. A medicine contains a drug as its **active ingredient**. Besides it contains some additional chemicals which make the drug suitable for its use as medicine. Medicines are used in diagnosis, prevention and treatment of a disease.

Drugs being foreign substances in a body, often give rise to undersirable, adverse side effects.

Drug design is an important branch of medicinal chemistry which aims at synthesis of new molecules having better biological response. There is an increasing trend in the current research in medicinal chemistry to take cognizance of traditional medical knowledge such as Ayurvedic medicine or natural materials to discover new drugs.

In this section, we consider some simple compounds having medicinal properties and active ingredients of some natural materials those are traditionally known to possess medicinal properties.

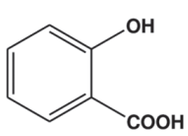
Do you know ?

The drug manufacturing companies usually have a patent for drugs which are sold with the brand name. After the expiry of patent the drug can be sold in the name of its active ingredient. These are called generic medicines.

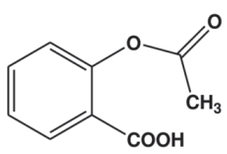
16.2.1 Analgesics and antipyretics

'Algesis' is a Greek word meaning 'feeling of pain.' Drugs which give relief from pain are called analgesics. About half of the analgesics are anti-inflammatory drugs, which kill pain by reducing inflammation or swelling. Antipyretics are used to reduce fever.

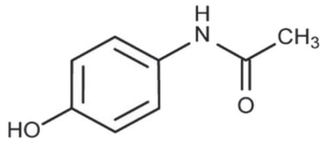
Pain-killing and fever reducing properties of an extract of bark of willow plant (commonly found in Europe) have been known for centuries. In nineteenth century its active ingredient, **salicylic acid** (2-hydroxybenzoic acid) was isolated and purified. The compound **aspirin** which is acetyl derivative of salicylic acid was found to have a fewer side effects than salicylic acid. It is one of the most widely used analgesic to date. It however, retains stomach irritating side effects of salicylic acid. A less problematic pain-killer is **paracetamol**, which is a phenol.



Salicylic acid



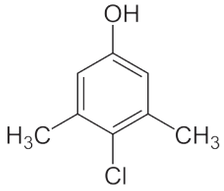
Aspirin (prodrug)



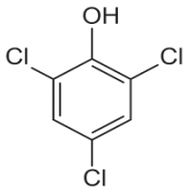
Molecular structure of paracetamol

16.2.2 Antimicrobials : The name **antimicrobial** is an umbrella term for any drug that inhibits or kills microbial cells that include bacteria, fungi and viruses. **Disinfectants** are non-selective antimicrobials, which kill a wide range of microorganisms including bacteria. Disinfectants are used on non-living surfaces for example, floors, instruments, sanitary ware and many others. **Antiseptics** are used to sterilise surfaces of living tissue when the risk of infection is very high, such as during surgery, on wounds and so on. **Antibiotics** are a type of antimicrobial designed to target bacterial infections within or on the body.

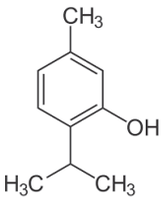
a. Antiseptics and disinfectants : Commonly used antiseptics include **inorganics** like iodine and boric acid or **organics** like iodoform and some phenolic compounds. Tincture of iodine (a 2 - 3 percent solution of iodine in alcohol- water mixture) and iodoform serve as powerful antiseptics and find use to apply on wounds. A dilute aqueous solution of boric acid is a weak antiseptic used for eyes. Various phenols are used as antiseptics and disinfectants. A dilute aqueous solution of phenol (known as **carbolic acid**) was one of the first antiseptic used in medicine in the late nineteenth century. It was however, found to be corrosive. Many chloro derivatives of phenols have been realized as more potent antiseptics than the phenol itself. They can be used with much lower concentrations, which reduce their corrosive effects. Two of the most common phenol derivatives in use are trichlorophenol (TCP) and chloroxylenol. The latter is the active ingredient (4.8 % W/V) of the popular antiseptic dettol. The other ingredients of dettol are isopropyl alcohol, pine oil, castor oil soap, caramel and water. Thymol obtained from oil of thyme (a spice plant) is an excellent non-toxic antiseptic. The p-chlorobenzyl phenol is used as disinfectant in all purpose cleaners.



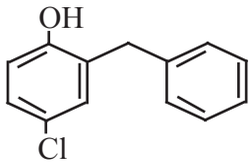
Chloroxylenol



2, 4, 6 Trichlorophenol

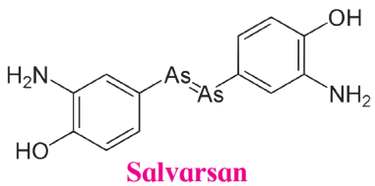


Thymol

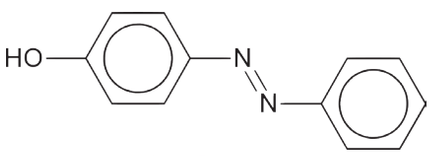


p - Chloro - o - benzylphenol

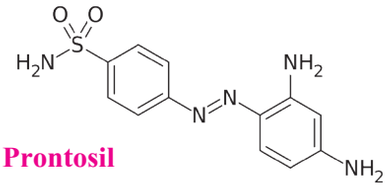
b. Antibiotics : Antibiotics are purely synthetic or obtained from microorganisms (bacteria, fungi or molds). Arsenic compounds were known to be highly poisonous to humans since long. **Paul Ehrlich,** German bacteriologist investigated arsenic based organic compounds in order to produce less toxic substances for the treatment of syphillis. He discovered the first effective treatment of syphilis, the synthetic antibiotic named **salvarsan**. He was awarded the Nobel prize for medicine (1908) for this discovery. Ehrlich noticed similarity in the structures of salvarsan and azodyes. With further investigations he succeded in synthesis of an effective diazo antibacterial, prontosil, in 1932. Subsequently it was discovered that prontosil gets converted into a simpler compound sulphanilamide in our body. This gave further direction to research in drug design which led to discovery of a wide range of sulpha drugs, analogues to sulphanilamide. One of the most effective being **sulphapyridine**.



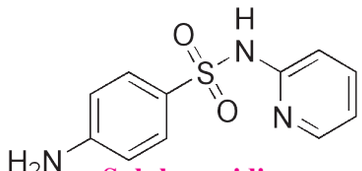
Salvarsan



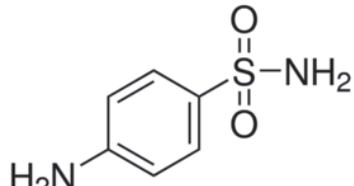
Azodye



Prontosil

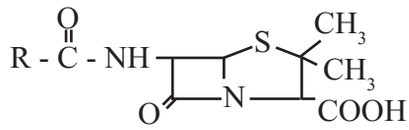


Sulphapyridine

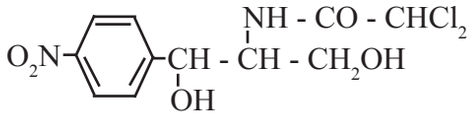


Sulphanilamide

In 1929, **Alexander Fleming** discovered the antibacterial properties of a penicillium fungus. The clinical utility of the purified active ingredient penicillin as antibiotic drug was established in the next thirteen years. This is the first antibiotic of microbial origin. Chloramphenicol, isolated in 1947 is another antibiotic of microbial origin.



General structure of penicillin



Chloramphenicol

Antibiotics can be of three types : broad spectrum (effective against wide range of bacteria), narrow spectrum (effective against one group of bacteria) or limited spectrum (effective against single organism).

A disadvantage of broad spectrum antibiotics is that they also kill the useful bacteria in the alimentary canal. Today many broad spectrum, narrow spectrum and limited spectrum antibiotics are known. They are synthetic, semisynthetic or of microbial origin.

6.2.3 Traditional knowledge in medicine

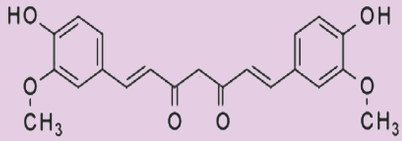
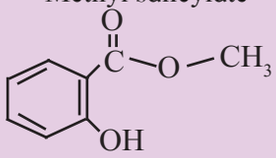
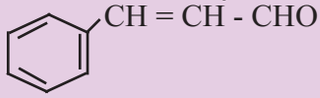
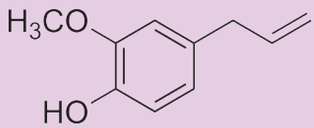
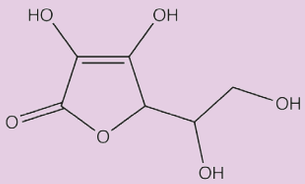
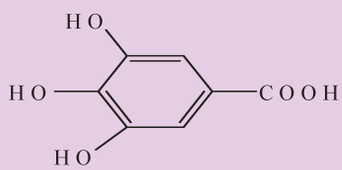
Do you know ?

The turmeric patent battle :

India won the legal battle against US patent and Trademark office (PTO) in 1997 and protected its intelectual property of traditional Indian knowledge about turmeric against patenting. Dr. Raghunath Mashelkar, the then Director General of the Council of Scientific and Industrial Research, New Delhi, India, led this case and upheld the national pride. In this long battle the CSIR argued that turmeric, a native Indian plant, had been used for centuries by its people for wound healing.

Since ancient times, in India, many *grandma remedies* are practised for curing ailments. The ancient medicinal system of India has documented medicinal uses of innumerable Indian plants. There is an increasing trend in the modern medicinal chemistry to make use of the traditional knowledge from various parts of world, to isolate active ingredients from medicinal plants and further develop new drugs. Table 16.2 enlists a few medicinal plants, their medicinal property and active ingredients therein.

Table 16.2 Active ingredients of some medicinal plants

Plant	Medicinal property	Name and structure of the active ingredient
Turmeric	antiseptic	Curcumin 
Wintergreen	analgesic	Methyl salicylate 
Cinnamon	antimicrobial for colds	Cinnamaldehyde 
Clove	antimicrobial, analgesic	Eugenol 
Citrus fruits	antioxidant	Vitamin C (ascorbic acid) 
Indian gooseberry (amla)	antidiabetic, antimicrobial antioxidant	Vitamin C, Gallic acid 

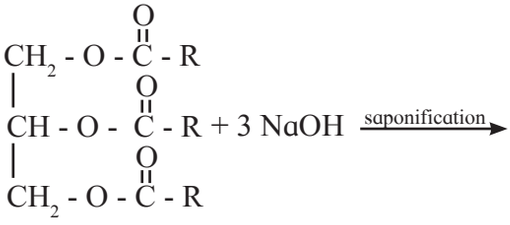
16.3 Cleansing Agents : Cleansing agents are substances which are used to remove stain, dirt or clutter on surfaces. They may be natural or synthetically developed.

Can you tell?

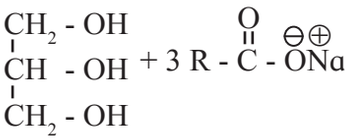
- Can we use the same soap for bathing as well as cleaning utensils or washing clothes ? Why ?
- How will you differentiate between soaps and synthetic detergent using borewell water?

16.3.1 Types of cleansing agents : Commercially cleansing agents are mainly of two types depending upon chemical composition : **soaps** and **synthetic detergents**.

a. Soaps : Soaps are sodium or potassium salts of long chain fatty acids. They are obtained by alkaline hydrolysis of natural oils and fats with NaOH or KOH. This is called **saponification** reaction. Chemically oils are triesters of long chain fatty acids and propan-1,2,3-triol commonly known as **glycerol** or **glycerin**. Saponification of oil produces soap and glycerol.



oil/fat



glycerin soap

The quality of soap depends upon the nature of oil and alkali used. Potassium soaps are soft to skin. Therefore toilet soaps are prepared by using better grades of oil and KOH. Care is taken to remove excess of alkali. Laundary soaps are made using NaOH. These also contain fillers like sodium rosinate (a lathering agents), sodium silicate, borax, sodium and trisodium phosphate.

Hard water and soap : Soaps are water soluble. They form scum in hard water and become inactive. This is because hard water contains dissolved salts of calcium and magnesium, which react with soap, precipitating calcium or magnesium salt of fatty acid (scum) which sticks to fabric.

$$2\ R - COONa\ (aq) + CaCl_2(aq) \longrightarrow (R - COO)_2Ca(s) + 2NaCl(aq)$$

Washing soda (Na_2CO_3) precipitates the dissolved calcium salts as carbonate and helps the soap action by softening of water.

b. Synthetic detergents : Synthetic detergents are man made cleansing agents designed to use even in hard water. There are three types of synthetic detergents, anionic detergents, cationic detergents and nonionic detergents. i. Anionic detergents are sodium salts of long chain alkyl sulfonic acids or long chain alkyl substituted benzene sulphonic acids. ii. Cationic detergents are quaternary ammonium salts having one long chain alkyl group. iii. Nonionic detergents are ethers of polyethylene glycol with alkyl phenol or esters of polyethylene glycol with long chain fatty acid. Table 16.3 displays some syntheic detergents.

Mechanism of cleansing action : Soaps and detergents bring about cleansing of dirty, greasy surfaces by the same mechanism. Dirt is held at the surface by means of oily matter and, therefore, cannot get washed with water. The molecules of soaps and detergent have two parts. One part is polar (called head) and the other part is long nonpolar chain of carbons (called tail).

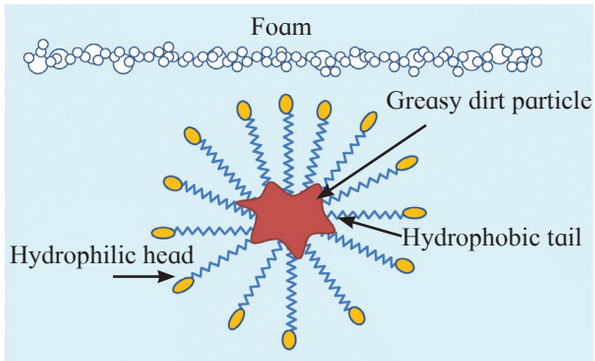


Fig. 16.2 : Soap micelle at work

The polar head (**hydrophilic**) can dissolve in water which is polar solvent. The nonpolar tail (**hydrophobic**) dissolve in oil/fat/grease. The molecules of soap/detergent are arranged around the oily droplet such that the nonpolar tail points towards the central oily drop while the polar head is directed towards the water. (see Fig. 16.2) Thus, micelles of soap/detergent are formed surrounding the oil drops, which are removed in the washing process.

Table 16.3 Synthetic detergents

Type	Example	Use
Anionic detergent	(sodium lauryl sulphate) $CH_3(CH_2)_{10}CH_2OSO_3^{\ominus}Na^{\oplus}$	Household detergent, additive in toothpaste
Cationic detergent	$CH_3(CH_2)_{15}\text{-}N^{\oplus}(CH_3)_3Br^{\ominus}$ (cetyltrimethyl ammonium bromide)	hair conditioner, germicide
Nonionic detergent	$CH_3(CH_2)_{16}$- COO $(CH_2CH_2O)n\ CH_2\ CH_2OH$ (an ester)	liquid dishwash
	C_9H_{19}–C$_6$H$_4$–O - $(CH_2CH_2O)_nCH_2CH_2OH$ (an ether)	liquid detergent

Exercises

1. Choose correct option

A. Oxidative Rancidity is ..... reaction
   a. addition b. subtitution
   c. Free radical d. combination

B. Saponification is carried out by .....
   a. oxidation b. alkaline hydrolysis
   c. polymarisation
   d. Free radical formation

C. Aspirin is chemically named as .....
   a. Salicylic acid
   b. acetyl salicylic acid
   c. chloroxylenol d. thymol

D. Find odd one out from the following
   a. dettol b. chloroxylenol
   c. paracetamol d. trichlorophenol

E. Arsenic based antibiotic is
   a. Azodye b. prontosil
   c. salvarsan d. sulphapyridine

F. The chemical used to slow down the browning action of cut fruit is
   a. SO_3 b. SO_2
   c. H_2SO_4 d. Na_2CO_3

G. The chemical is responsible for the rancid flavour of fats is
   a. Butyric acid b. Glycerol
   c. Protein d. Saturated fat

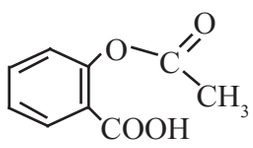
H. Health benefits are obtained by consumption of
   a. Saturated fats
   b. trans fats
   c. mono unsaturated fats
   d. all of these

2. Explain the following :

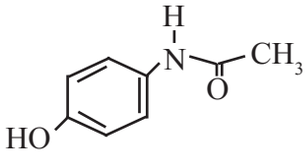
A. Cooking makes food easy to digest.
B. On cutting some fruits and vegetable turn brown.
C. Vitmin E is added to packed edible oil.
D. Browning of cut apple can be prolonged by applying lemon juice.
E. A diluted solution (4.8 % w/v) of 2,4,6-trichlorophenol is employed as antiseptic.
F. Turmeric powder can be used as antiseptic.

3. Identify the functional grops in the following molecule :

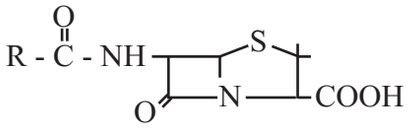
A. Aspirin



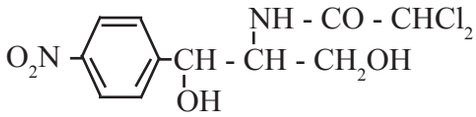
B. Paracetamol



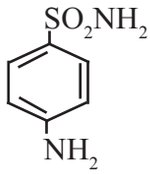
C. Penicillin



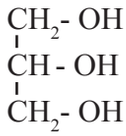
D. Chloramphenicol



E. Sulphanilamide



F. Glycerin



4. Give two differences between the following

A. Disinfectant and antiseptic
B. Soap and synthetic detergent
C. Saturated and unsaturated fats
D. Rice flour and cooked rice

5. Match the pairs.

A group	B group
A. Paracetamol	a. Antibiotic
B. Chloramphenicol	b. Synthetic detergent
C. BHT	c. Soap
D. Sodium stearate	d. Antioxidant
	e. Analgesic

6. Name two drugs which reduce body pain.

7. Explain with examples

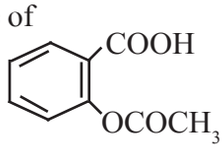
A. Antiseptics
B. Disinfectant
C. Cationic detergents
D. Anionic detergents
E. Non-ionic detergents

8. Explain : mechanism of cleansing action of soap with flow chart.

9. What is meant by broad spectrum antibiotic and narrow spectrum antibiotics?

10. Answer in one senetence

A. Name the painkiller obtained from acetylation of salicyclic acid.
B. Name the class of drug often called as painkiller.
C. Who discovered penicillin?
D. Draw the structure of chloroxylenol and salvarsan.
E. Write molecular formula of Butylated hydroxy toluene.
F. What is the tincture of iodine ?
G. Draw the structure of BHT.
I. Write a chemical equation for saponification.
J. Write the molecular formula and name of



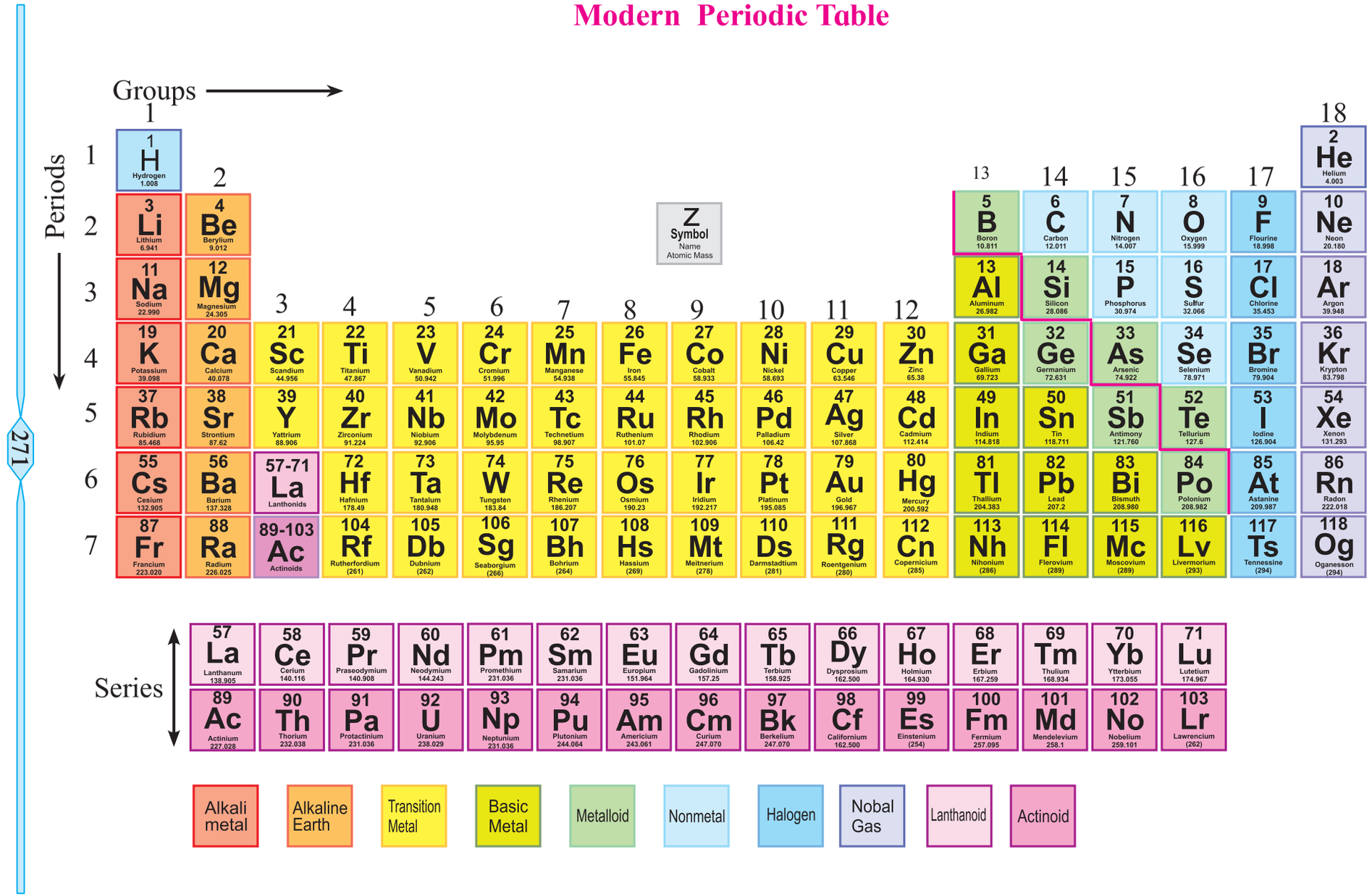
11. Answer the following

A. Write two examples of the following.
a. Analgesics
c. Antiseptics d. Antibiotics
e. Disinfectant
B. What do you understand by antioxidant ?

Activity :

Collect information about different chemical compounds as per their applications in day-to-day life.

Modern Periodic Table



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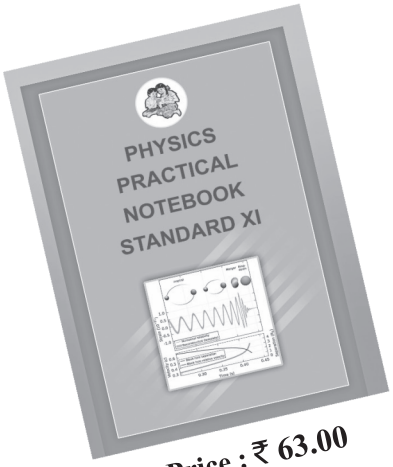

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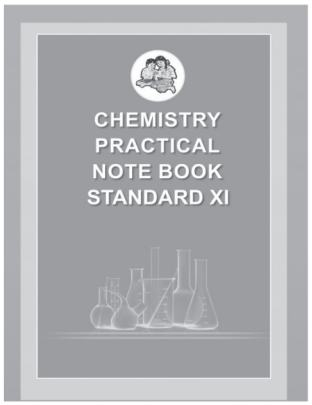

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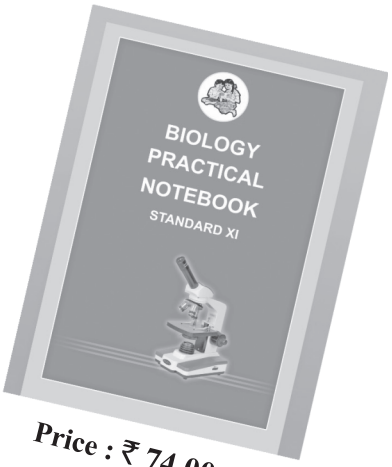

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- Separate space for writing answers

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