



THERMODYNAMICS

The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation is called Thermodynamics.

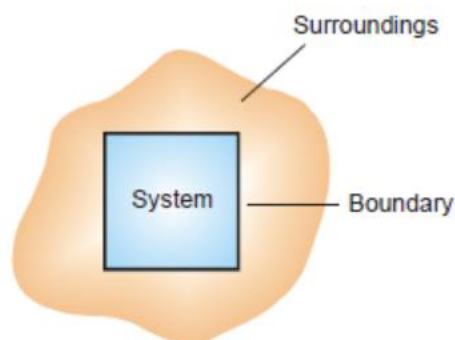
THE THREE EMPIRICAL LAWS

The study of thermodynamics is based on three broad generalisations derived from well established experimental results. These generalizations are known as the First, Second and Third law of thermodynamics.

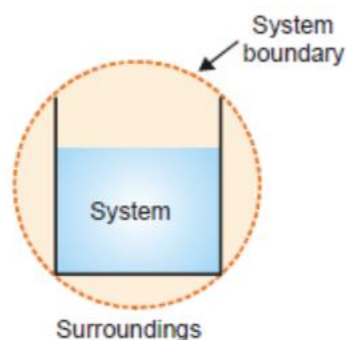
THERMODYNAMIC TERMS AND BASIC CONCEPTS:

SYSTEM, BOUNDARY, SURROUNDINGS

- A system is that part of the universe which is under thermodynamic study and the rest of the universe is surroundings.
- The real or imaginary surface separating the system from the surroundings is called the boundary.



Thermodynamic system.



Water contained in a beaker constitutes a system.

HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

When a system is uniform throughout, it is called a Homogeneous System. Examples are: a pure single solid, liquid or gas, mixtures of gases, and true solution of a solid in a liquid. A homogeneous system is made of one phase only. A phase is defined as a homogeneous, physically distinct and mechanically separable portion of a system.

A heterogeneous system is one which consists of two or more phases. In other words it is not uniform throughout. Examples of heterogeneous systems are : ice in contact with water, ice in contact with vapour etc. Here ice, water and vapour constitute separate phases.



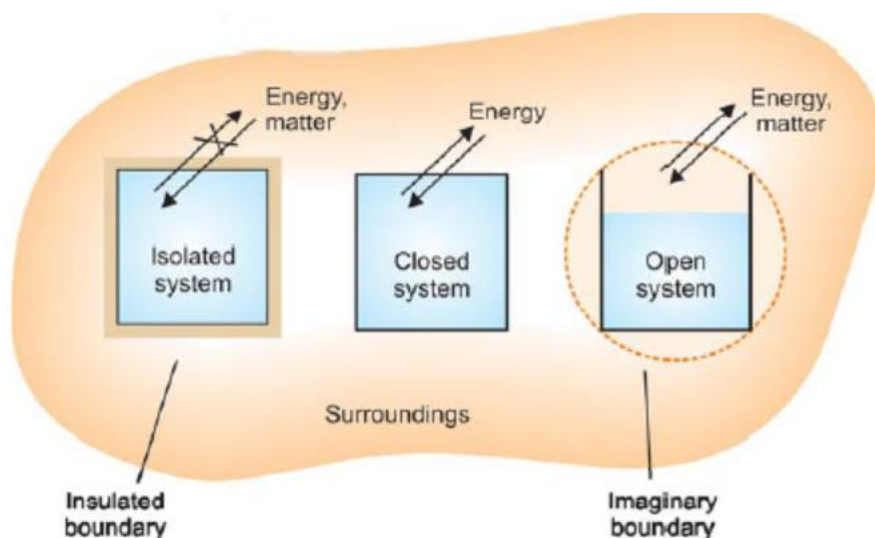
TYPES OF THERMODYNAMIC SYSTEMS

There are three types of thermodynamic systems depending on the nature of the boundary. If the boundary is closed or sealed, no *matter* can pass through it. If the boundary is insulated, no *energy* (say heat) can pass through it.

(1) Isolated System

When the boundary is both sealed and insulated, no interaction is possible with the surroundings. Therefore, an isolated system is one that can transfer neither matter nor energy to and from its surroundings.

A substance, say boiling water, contained in a *thermos flask*, is an example of an isolated system



Three types of thermodynamic systems.

(2) Closed System

Here the boundary is sealed but not insulated. Therefore, a closed system is one which cannot transfer matter but can transfer energy in the form of heat, work and radiation to and from its surroundings.

A specific quantity of hot water contained in a sealed tube, is an example of a closed system.

(3) Open System

In such a system the boundary is open and un-insulated. Therefore, an open system is one which can transfer both energy and matter to and from its surroundings.

Hot water contained in a beaker placed on laboratory table is an open system.

(4) Adiabatic Systems

Those systems, in which no thermal energy passes into or out of the system, are said to be adiabatic systems.



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PAGE 3 OF 18

Edition : 1

INTENSIVE AND EXTENSIVE PROPERTIES

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes:

- (a) Intensive properties
- (b) Extensive properties

(a) Intensive Properties

A property which does not depend on the quantity of matter present in the system is known as Intensive Property.

Some examples of intensive properties are *pressure, temperature, density, and concentration.*

(b) Extensive Properties

A property that does depend on the quantity of matter present in the system is called an Extensive Property.

Some examples of extensive properties are *volume, number of moles, enthalpy, entropy, and Gibbs' free energy.*

THERMODYNAMIC PROCESSES

When a thermodynamic system changes from one state to another, the operation is called a Process. These processes involve the change of conditions (temperature, pressure and volume).

The various types of thermodynamic processes are:

(1) Isothermal Processes

Those processes, in which the temperature remains fixed, are termed isothermal processes.

For an isothermal process $dT = 0$

(2) Adiabatic Processes

Those processes in which no heat can flow into or out of the system, are called adiabatic processes.

For an adiabatic process $dq = 0$

(3) Isobaric Processes

Those processes which take place at constant pressure are called isobaric processes.

For an isobaric process $dp = 0$

(4) Isochoric Processes

Those processes in which the volume remains constant are known as isochoric processes.

For isochoric processes $dV = 0$.

(5) Cyclic Process

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.

For a cyclic process $dE = 0, dH = 0$.

REVERSIBLE AND IRREVERSIBLE PROCESSES

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COPY :
PAGE 4 OF 18

Edition : 1

A thermodynamic reverse process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.

When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, it is said to be an irreversible process.

DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

S.No	Reversible Process	Irreversible Process
1.	It takes place in infinite number of infinitesimally small steps and it would take <i>infinite time</i> to occur.	It takes place <i>infinite time</i> .
2.	It is <i>imaginary</i> as it assumes the presence of frictionless and weightless piston.	It is <i>real</i> and can be performed actually.
3.	It is in equilibrium state at <i>all stages</i> of the operation.	It is in equilibrium state only at the <i>initial and final stages</i> of the operation.
4.	All changes are <i>reversed</i> when the process is carried out in reversible direction.	After this type of process has occurred all changes <i>do not return</i> to the initial state by themselves.
5.	It is extremely slow.	It proceeds at <i>measureable speed</i> .
6.	Work done by a reversible process is <i>greater</i> than the corresponding	Work done by a irreversible process is <i>smaller</i> than the corresponding reversible process.

NATURE OF HEAT AND WORK

When a change in the *state* of a system occurs, energy is transferred to or from the surroundings.

This energy may be transferred as heat or mechanical work.

We shall refer the term 'work' for mechanical work which is defined as force × distance.

Unit of Work: joule

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COPY :
PAGE 5 OF 18

Edition : 1

1 joule = 10⁷ ergs

or 1 erg = 10⁻⁷ J

We often use kilojoule (kJ) for large quantities of work 1 kJ = 1000 J

Units of Heat

The unit of heat, which was used for many years, is calorie (cal).

Sign Convention of Heat:

The symbol of heat is q . If the heat flows from the surroundings into the system to raise the energy of the system, it is taken to be positive, $+q$. If heat flows from the system into the surroundings, lowering the energy of the system, it is taken to be negative, $-q$.

q is (+) q is (-)

Sign Convention of Work

The symbol of work is w . If work is done on a system by the surroundings and the energy of the system is thus increased, it is taken to be positive, $+w$. If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, $-w$.

Summary of Sign Conventions

Heat flows into the system, q is +ve Heat flows out of the system, q is -ve

Work is done on the system, w is +ve Work is done by the system, w is -ve

INTERNAL ENERGY

A thermodynamic system containing some quantity of matter has within itself a definite quantity of energy. This energy includes not only the translation kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies. The kinetic and potential energy of the nuclei and electrons within the individual molecules also contribute to the energy of the system.

The total of all the possible kinds of energy of a system, is called its Internal Energy.

The internal energy of a system, like temperature, pressure, volume, etc., is determined by the state of a system and is independent of the path by which it is obtained. Hence internal energy of a system is a state function.

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is, known as the Law of Conservation of Energy to the thermodynamic system. It states that: " the total energy of an isolated system remains constant though it may change from one form to another".

Mathematical statement of the First Law as :

$$\Delta E = q - w \dots(1)$$

where q = the amount of heat supplied to the system

w = work done by the system

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COPY :
PAGE 6 OF 18

Edition : 1

Thus First Law may also be stated as : the net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.

SOLVED PROBLEM: Find ΔE , q and w if 2 moles of hydrogen at 3 atm pressure expand isothermally at 50°C and reversibly to a pressure of 1 atm.

SOLUTION

Since the operation is isothermal and the gas is ideal

$$\Delta E = 0$$

From the First Law

$$\Delta E = q - w$$

$$\therefore q - w = 0$$

$$\text{when } \Delta E = 0$$

$$\text{or } q = w$$

For a reversible process

$$w = -nRT \ln (P_1/P_2) \text{ or } -2.303 nRT \log P_1/P_2$$

$$= -2 \times 1.987 \times 323 \times 2.303 \times \log 3$$

$$= -1410 \text{ cal}$$

Since $q = w$

$$q = -1410 \text{ cal}$$

SOLVED PROBLEM:

1g of water at 373 K is converted into steam at the same temperature. The volume of water becomes 1671 ml on boiling. Calculate the change in the internal energy of the system if the heat of vaporization is 540 cal/g.

SOLUTION

As the vaporization takes place against a constant pressure of 1 atmosphere, work done for an irreversible process, w , is

$$w = P (V_2 - V_1)$$

$$= nRT$$

$$= 1/18 \times 1.987 \times 373$$

$$= 41 \text{ cal/g}$$

Now

$$q = 540 \text{ cal/g}$$

Since

$$\Delta E = q - w \text{ (First Law)}$$

$$= 540 - 41$$

$$\therefore \Delta E = 499 \text{ cal/g}$$

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PAGE 7 OF 18

Edition : 1

SOLVED PROBLEM: A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J thermal energy from its surroundings. Determine ΔE for the process.

SOLUTION

$$\Delta E = q - w \dots(1)$$

Here $q = 400 \text{ J}$

$$w = -P(V_2 - V_1) = - (1) (10 - 5)$$

$$= - 5 \text{ l atm}$$

$$= - 506 \text{ J} [1 \text{ l atm} = 101.2 \text{ J}]$$

Substituting values in (1)

$$\Delta E = 400 \text{ J} - (- 506 \text{ J})$$

$$= 400 \text{ J} + 506 \text{ J}$$

$$= 906 \text{ J}$$

ENTHALPY OF A SYSTEM

In a process carried at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy (E), as no PV work is done. But in a constant-pressure process, the system (a gas) also expends energy in doing PV work. Therefore, the total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called the Enthalpy of the system and is represented by the symbol H . Thus enthalpy is defined by the equation:

$$H = E + PV \dots(1)$$

Change in Enthalpy

If ΔH be the difference of enthalpy of a system in the final state (H_2) and that in the initial state (H_1),

$$\Delta H = H_2 - H_1 \dots(2)$$

Substituting the values of H_2 and H_1 , as from (1) and (2), we have

$$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$= (E_2 - E_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta E + \Delta PV$$

If P is constant while the gas is expanding, we can write

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

Or $\Delta H = \Delta E + w$ ($w = \text{work}$) $\dots(3)$

According to the First Law,

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COPY :
PAGE 8 OF 18

Edition : 1

$$\Delta E = q - w \quad \dots(4)$$

where q = heat transferred

From equations (3) and (4)

$\Delta H = q$ when change in state occurs at constant pressure

This relationship is usually written as $\Delta H = qp$

where subscript p means constant pressure.

Thus ΔH can be measured by measuring the heat of a process occurring at constant pressure.

Relation Between ΔH and ΔE :

Calorific values of many gaseous fuels are determined in constant volume calorimeters. These values are, therefore, given by the expression,

$$qv = \Delta E$$

When any fuel is burnt in the open atmosphere, additional energy of expansion, positive or negative, against the atmosphere is also involved. The value of q thus actually realised, *i.e.*, $qp = \Delta H$, may be different from the equation,

$$\Delta H = \Delta E + P\Delta V \quad \dots(1)$$

If gases are involved in a reaction, they account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison. Suppose we have n_1 moles of gases before reaction, and n_2 moles of gases after it. Assuming ideal gas behaviour, we have

$$P V_2 = n_2 RT$$

$$P V_1 = n_1 RT$$

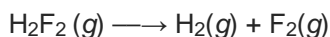
$$\therefore P(V_2 - V_1) = (n_2 - n_1) RT$$

$$\text{or } P\Delta V = \Delta n RT$$

Substituting in equation (1) we have,

$$\Delta H = \Delta E + \Delta n RT$$

SOLVED PROBLEM. For the reaction



$$\Delta E = -14.2 \text{ kcal/mole at } 25^\circ \text{C}$$

Calculate ΔH for the reaction.

SOLUTION

$$\Delta H = \Delta E + \Delta n RT$$

$$\Delta n = n_2 - n_1$$



Now

$$n_2 = 1 + 1 = 2$$
$$n_1 = 1$$
$$n_2 - n_1 = 2 - 1 = 1$$
$$\Delta H = \Delta E + 1 \times 1.987 \times 298/1000$$
$$= -14.2 + 0.592$$
$$= -13.6 \text{ kcal/mole}$$

MOLAR HEAT CAPACITIES

By heat capacity of a system we mean the capacity to absorb heat and store energy. As the system absorbs heat, it goes into the kinetic motion of the atoms and molecules contained in the system. This increased kinetic energy raises the temperature of the system. If q calories is the heat absorbed by mass m and the temperature rises from T_1 to T_2 , the heat capacity (c) is given by the expression

$$c = \frac{q}{m \times (T_2 - T_1)} \quad \dots(1)$$

Thus heat capacity of a system is the heat absorbed by unit mass in raising the temperature by one degree (K or $^\circ C$) at a specified temperature. When mass considered is 1 mole, the expression (1) can be written as

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \quad \dots(2)$$

where C is denoted as Molar heat capacity.

The molar heat capacity of a system is defined as the amount of heat required to raise the temperature of one mole of the substance (system) by 1 K. Since the heat capacity (C) varies with temperature; its true value will be given as

$$C = \frac{dq}{dT}$$

where dq is a small quantity of heat absorbed by the system, producing a small temperature rise dT .

Thus the molar heat capacity may be defined as the ratio of the amount of heat absorbed to the rise in temperature.

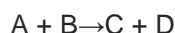
Units of Heat Capacity

The usual units of the molar heat capacity are calories per degree per mole ($\text{cal K}^{-1} \text{mol}^{-1}$), or joules per degree per mole ($\text{J K}^{-1} \text{mol}^{-1}$), the latter being the SI unit. Heat is not a state function, neither is heat capacity.

EXOTHERMIC AND ENDOTHERMIC REACTIONS



Let us consider a general reaction at constant pressure,



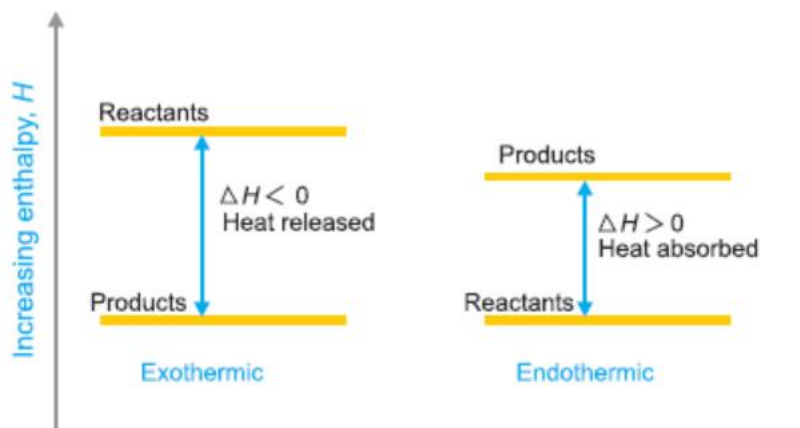
If H_A , H_B , H_C and H_D be the enthalpies of A, B, C and D respectively, the heat of reaction at constant pressure viz., ΔH is equal to the difference in enthalpies of the products and the reactants i.e.,

$$\begin{aligned} \Delta H &= H_{\text{products}} - H_{\text{reactants}} \\ &= (H_C + H_D) - (H_A + H_B) \end{aligned}$$

The value of ΔH may be either zero, negative or positive. Where ΔH is zero, the enthalpies of the products and reactants being the same, the heat is evolved or absorbed. In case ΔH is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.

Such reactions which are accompanied by the evolution of heat energy are called Exothermic reactions.

When ΔH is positive, the enthalpy or heat content of the reactants and an equivalent of heat is absorbed by the system from the surroundings.



Enthalpy diagram for an exothermic and endothermic reaction.

Such reactions which are accompanied by absorption of heat are called Endothermic reactions.

Thus for an exothermic reaction $H_p < H_r$ and $\Delta H = -ve$, for an endothermic reaction $H_p > H_r$ and $\Delta H = +ve$.

Examples of endothermic and exothermic process:

Exothermic processes

- Making ice cubes
- Formation of snow in clouds
- Condensation of rain from water vapours

Endothermic processes

- Melting ice cubes
- Conversion of frost to water vapour
- Evaporation of water



DIFFERENCE BETWEEN EXOTHERMIC AND ENDOTHERMIC REACTIONS:

Endothermic reaction	Exothermic reaction
1. In endothermic reaction heat is absorbed from surroundings.	1. In exothermic reaction heat is given out to surroundings.
2. Sum of enthalpies of products is greater than sum of enthalpies of reactants i.e. $\Sigma_p H > \Sigma_R H$	2. Sum of enthalpies of products is less than sum of enthalpies of reactants. i.e. $\Sigma_p H < \Sigma_R H$
3. Heat of reaction, ΔH is positive.	3. Heat of reaction, ΔH is negative.
4. Products are less stable than reactants.	4. Products are more stable than reactants.
5. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -394 \text{ kJ}$	5. $N_{2(g)} + O_{2(g)} \rightarrow 2NO$ $\Delta H = +180 \text{ kJ}$

SPONTANEOUS PROCESSES AND NON-SPONTANEOUS:

A process which proceeds of its own accord, without any outside assistance, is termed a spontaneous or natural process.

The reverse process which does not proceed on its own, is referred to as a non spontaneous or unnatural process.

In general, the tendency of a process to occur naturally is called the spontaneity.

CRITERIA OF SPONTANEITY

Some important criteria of spontaneous physical and chemical changes are listed below.

- (1) A spontaneous change is one-way or unidirectional. For reverse change to occur, work has to be done.
- (2) For a spontaneous change to occur, time is no factor. A spontaneous reaction may take place rapidly or very slowly.
- (3) If the system is not in equilibrium state (unstable), a spontaneous change is inevitable. The change will continue till the system attains the state of equilibrium.
- (4) Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed. To take the system away from equilibrium, some external work must be done on the system.
- (5) A spontaneous change is accompanied by decrease of internal energy or enthalpy (ΔH).

ENTROPY



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COPY :
PAGE 12 OF 18

Edition : 1

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

The symbol of entropy is S , while the change in disorder accompanying a process from start to completion is represented by ΔS . The entropy of a system is a state function and depends only on the initial and final states of the system. The change in entropy, ΔS , for any process is given by the equation,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When $S_{\text{final}} > S_{\text{initial}}$, ΔS is positive.

A process accompanied by an increase in entropy tends to be spontaneous.

Numerical definition of entropy:

Entropy could be precisely defined as: for a reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temperature (T). That is,

$$\Delta S = q / T$$

If heat is absorbed, then ΔS is positive and there will be increase in entropy. If heat is evolved, ΔS is negative and there is a decrease in entropy.

STANDARD ENTROPY:

The absolute entropy of a substance at 25°C (298 K) and one atmosphere pressure is called the standard entropy; S° .

Once we know the entropies of a variety of substances, we can calculate the standard entropy change, ΔS° , for chemical reactions.

$$\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$$

STATEMENT OF THE SECOND LAW

The second law of thermodynamics states that: whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe. More specifically, we take the term 'universe' to mean the system and the surroundings. Thus,

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

- The second law, as stated above, tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases. In other words $\Delta S_{\text{univ}} > 0$.
- When a reversible process occurs, the entropy of the system remains constant. $\Delta S_{\text{univ}} = 0$.
- Since the entire universe is undergoing spontaneous change, the second law can be most generally and concisely stated as: the entropy of the system is constantly increasing.

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COPY :
PAGE 13 OF 18

Edition : 1

CHEMICAL KINETICS

The branch of Physical chemistry which deals with the rate of reactions is called Chemical Kinetics. The study of Chemical

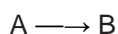
Kinetics includes:

- (1) The rate of the reactions and rate laws.
- (2) The factors as temperature, pressure, concentration and catalyst that influences the rate of a reaction.
- (3) The mechanism or the sequence of steps by which a reaction occurs.

The knowledge of the rate of reactions is very valuable to understand the chemical of reactions. It is also of great importance in selecting optimum conditions for an industrial process so that it proceeds at a rate to give maximum yield.

REACTION RATE

The rate of a reaction tells as to what speed the reaction occurs. Let us consider a simple reaction



The concentration of the reactant A decreases and that of B increases as time passes. The **rate of reactions is defined as the change in concentration of any of reactant or products per unit time**. For the given reaction the rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B.

Thus rate of reaction = rate of disappearance of A

= rate of appearance of B

$$\text{or rate} = - \frac{d[A]}{dt}$$

$$= + \frac{d[B]}{dt}$$

where [] represents the concentration in moles per litre whereas 'd' represents infinitesimally small change in concentration. Negative sign shows the concentration of the reactant A decreases whereas the positive sign indicates the increase in concentration of the product B.

UNITS OF RATE

Reactions rate has the units of concentration divided by time. We express concentrations in moles per litre (mol/litre or mol/l or mol l⁻¹) but time may be given in any convenient unit second (s), minutes (min), hours (h), days (d) or possible years. Therefore, the units of reaction rates may be,

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REV. NO. : **R0**
DATE : **05/04/2021**
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PAGE 14 OF 18

Edition : 1

mole/litre sec or mol 1^{-1} s
mole/litre min or mol 1^{-1} min $^{-1}$
mole/litre hour or mol 1^{-1} h $^{-1}$ and, so on

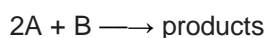
RATE LAWS

The rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.

Thus for a substance A undergoing reaction,

$$\text{rate} \rightarrow [A]^n$$
$$\text{or rate} = k [A]^n \dots(1)$$

For a reaction



the reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as

$$\text{rate} = k [A]^m [B]^n \dots(2)$$

Expressions such as (1) and (2) tell the relation between the rate of a reaction and reactant concentrations.

An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.

ORDER OF A REACTION

The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

$$\text{rate} = k [A]^m [B]^n \dots(1)$$

The order of such a reaction is $(m + n)$.

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n . The **overall order of reaction** $(m + n)$ may range from 1 to 3 and can be fractional.

Examples of reaction order:

Reactions may be classified according to the order. If in the rate law (1) above

- (i) $m + n = 1$, it is **first order reaction**
- (ii) $m + n = 2$, it is **second order reaction**
- (iii) $m + n = 3$, it is **third order reaction**

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RATE LAW	REACTION ORDER
$\text{rate} = k [\text{N}_2\text{O}_5]$	1
$\text{rate} = k [\text{H}_2] [\text{I}_2]$	$1 + 1 = 2$
$\text{rate} = k [\text{NO}_2]^2$	2
$\text{rate} = k [[\text{H}_2] [\text{NO}]^2]$	$1 + 2 = 3$
$\text{rate} = k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$	$1 + \frac{1}{2} = 1\frac{1}{2}$

MOLECULARITY OF A REACTION

Chemical reactions may be classed into two types :

- (a) Elementary reactions
- (b) Complex reactions

An **elementary reaction** is a simple reaction which occurs in a single step.

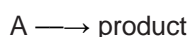
A **complex reaction** is that which occurs in two or more steps.

Molecularity of an Elementary Reaction

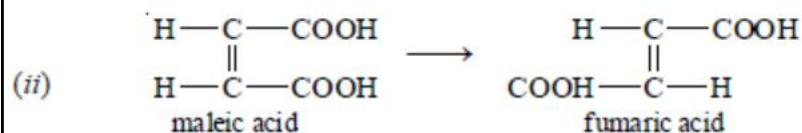
The molecularity of an elementary reaction is defined as: **the number of reactant molecules involved in a reaction.**

Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called **unimolecular, bimolecular and termolecular** respectively. Thus we have:

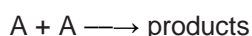
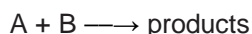
- (a) **Unimolecular reactions:** (molecularity = 1)



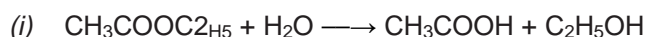
Examples are: (i) $\text{Br}_2 \longrightarrow 2\text{Br}$



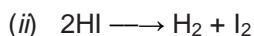
- (b) **Bimolecular reactions:** (molecularity = 2)



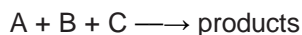
Examples are:



Ethyl acetate acetic acid ethyl alcohol



- (c) **Termolecular reactions :** (molecularity = 3)

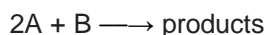


Examples are :



Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction.



$$\text{rate} \longrightarrow [A]^2 [B]$$

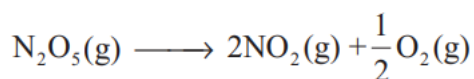
$$\text{or rate} = k [A]^2 [B] \text{ (rate law)}$$

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is $2 + 1 = 3$. The sum of powers in the rate law is $2 + 1$ and hence the reaction order is also 3. Thus **the molecularity and order for an elementary reaction are equal.**

S.NO	ORDER OF A REACTION	MOLECULARITY OF A REACTION
1	It is the sum of powers of the concentration terms in the rate law undergoing simultaneous collision in the rate law expression.	It is number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
2	It is an experimentally determined value.	It is a theoretical concept.
3	It can have fractional value.	It is always a whole number .
4	It can assume zero value .	It cannot have zero value .
5	Order of a reaction can change with the conditions such as pressure, temperature, concentration.	Molecularity is invariant for a chemical reaction.

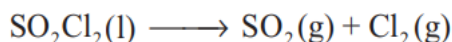
EXAMPLES FOR THE FIRST ORDER REACTION

(i) Decomposition of dinitrogen pentoxide

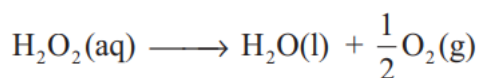




(ii) Decomposition of thionylchloride;



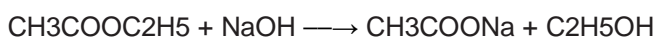
(iii) Decomposition of the H₂O₂ in aqueous solution;



(iv) Isomerisation of cyclopropane to propene.

EXAMPLES OF SECOND ORDER REACTION

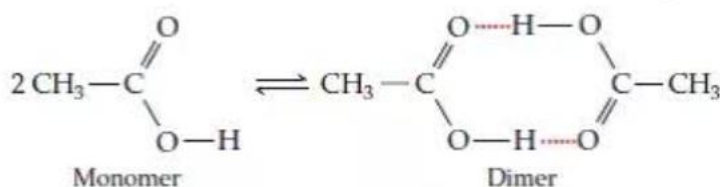
(i) Hydrolysis of an Ester by NaOH. This is typical second order reaction.



ethyl acetate

ethyl alcohol

(ii) Dimerisation reaction is an another example for second order reaction (dimerisation of acetic acid is shown below).



FACTORS AFFECTING THE REACTION RATE

The rate of a reaction is affected by the following factors.

1. Nature and state of the reactant
2. Concentration of the reactant
3. Surface area of the reactant
4. Temperature of the reaction
5. Presence of a catalyst

Nature and state of the reactant:

The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants. The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants. For example, reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

Concentration of the reactants:



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REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 18 OF 18

DOCUMENT TITLE

**UNIT –I
THERMODYNAMICS AND CHEMICAL KINETICS**

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The rate of a reaction increases with the increase in the concentration of the reactants. Higher the concentration, greater is the possibility for collision and hence the rate.

Effect of surface area of the reactant:

In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate. For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased. For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of CaCO₃ as marble.

Effect of presence of catalyst:

Significant changes in the reaction can be brought out by the addition of a substance called catalyst. A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change. They may participate in the reaction, but again regenerated and the end of the reaction.

EXCERCISE:

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REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 19 to 37

Edition : 1

CHROMATOGRAPHY

Chromatography can be defined as the technique for the separation of a mixture of compounds where the separation is brought about by the differential movement of the individual compounds through a porous medium under the influence of a moving solvent.

Chromatography is based on the general principle of distributing the components of a mixture of organic compounds between two phases – a stationary phase and a moving phase.

1. The stationary phase can be a solid or liquid supported on a solid, while the moving phase is a liquid or a gas.
2. When the stationary phase is a solid, the basis of separation is adsorption; when it is a liquid, the basis is partition.

The different chromatographic techniques used are:

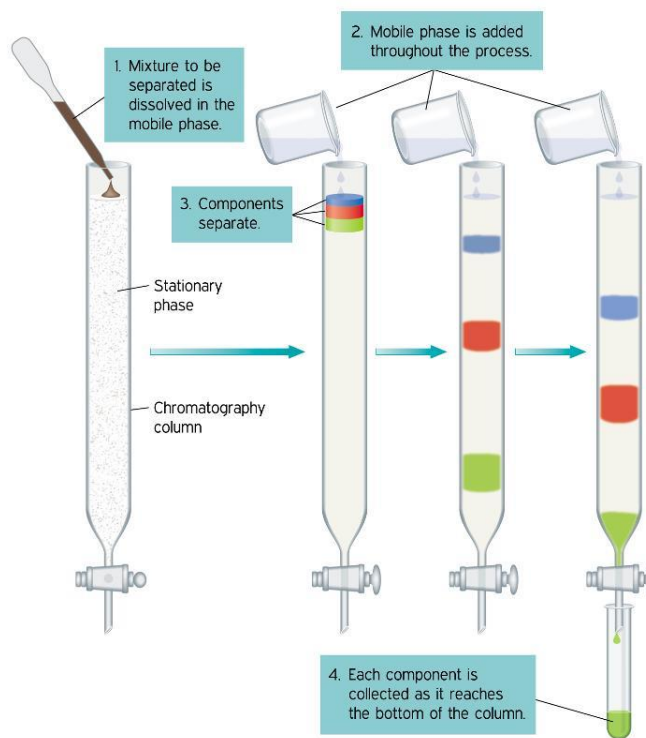
1. Column chromatography (CC),
2. Thin-layer chromatography (TLC),
3. paper chromatography (PC),
4. Gas-liquid chromatography (GLC) and ion-exchange chromatography.

a) Column Chromatography

- The simplest chromatographic method is column chromatography. It is carried out in a long glass column having a stop-cock near the bottom.
- To start the operation, a plug of cotton or glass wool is placed at the bottom of the column to support the adsorbent powder.
- The tube is packed uniformly with suitable adsorbent. This constitutes what is known as the stationary phase.
- The commonly employed adsorbents are activated aluminium oxide (alumina), magnesium oxide, silica gel and starch.
- A loose plug of cotton or glass wool is then placed at the top of the adsorbent column.

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- The substance to be purified is added, as such if it is a liquid or in the form of its solution in some suitable solvent if it is a solid, at the top of the column and allowed to pass slowly through it. As it passes through the column, the different components of a mixture (Say A, B and C) get adsorbed to different extent and are thus retained by the adsorbent at different levels of the column.
- The components which are adsorbed very strongly are retained at the top while others are retained at lower levels. In this way different zones or bands are formed in the column which contains different components of a mixture.
- As soon as the last portion of the substances enters the column, a selected solvent, known as eluent, is added to the column. This acts as moving phase.
- The elements dissolve out the different components from the various zones selectively and thus 'take out' the different bands in the form of fractions which are collected separately.

b) Thin Layer Chromatography (TLC)

- Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent.



- A thin layer (about 0.2mm thick) of an adsorbent (Silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate.
- The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate.
- The glass plate is then placed in a closed jar containing the solvent (Below 2cm height). As the solvent jar moves up the plate, the components of mixture move up along the plate to different distances depending on this degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retention factor ie., R_f Value

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

c) Paper Chromatography

It is an important and useful class of partition chromatography. In this technique, the stationary phase is considered to be made up of water molecules bound to the cellulose network (inert support) of the paper. The

mobile phase, known as the developing solvent consists of either one solvent or a mixture of different solvents. Separation of the mixture into pure compounds takes place by the partitioning of different compounds

between these two liquid phases. The mobile phase travels by capillary action through the paper.

Depending upon the way the solvent travels on the paper, there are three types of paper chromatography.

i) Ascending Paper Chromatography: The mobile phase moves upwards on the paper strip in this case.

ii) Descending Paper Chromatography: The mobile phase in this case moves downward on the paper strip.

iii) Circular or radial paper chromatography: The mobile phase moves horizontally along a circular sheet of paper in this case.

In the ascending paper chromatography, the mixture of compounds is applied on the paper as a spot little above the lower end and then this end is dipped in the solvent. When the solvent has raised



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REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 19 to 37

Edition : 1

more than two third length of the paper, then it is removed from the solvent. The paper is dried and is known as chromatogram.

Now the spots for different compounds can be visualised using some suitable chemicals. The ratio of the distance travelled by the compound in a particular solvent to that the distance travelled by the solvent is a constant and is known as retention factor (Rf). This value is used in identifying the compounds.

$$R_f = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the Solvent}}$$

Adsorption isotherm:

- It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature.
- Different adsorption isotherms have been Freundlich, Langmuir and BET theory.
 - Langmuir isotherm (adsorbed layer one molecule thick)
 - Freundlich isotherm (Heterogeneous adsorbent surface with different adsorption sites)
 - Brunauer, Emmertt and Teller (BET) isotherm (molecules can be adsorbed more than one layer thick)

LANGMUIR ADSORPTION ISOTHERM

Langmuir (1916) derived a simple adsorption isotherm based on theoretical considerations. It was named after him.

Langmuir made the following assumptions.

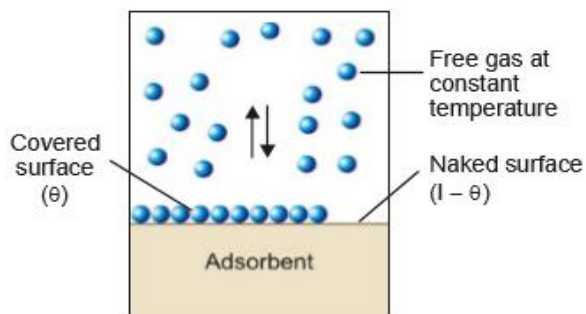
- (1) The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.
- (2) The adsorbed layer is uniform all over the adsorbent.
- (3) There is no interaction between the adjacent adsorbed molecules.

Derivation of Langmuir Isotherm

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some of these molecules then evaporate or are 'desorbed' fairly rapidly. A dynamic equilibrium is eventually established between the two opposing processes, adsorption and desorption.

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If θ is the fraction of the total surface covered by the adsorbed molecules, the fraction of the naked area is $(1 - \theta)$. The rate of desorption (R_d) is proportional to the covered surface θ . Therefore,

$$R_d = k_d \theta$$

where k_d is the rate constant for the desorption process.

The rate of adsorption (R_a) is proportional to the available naked surface $(1 - \theta)$ and the pressure (P) of the gas.

$$R_a = k_a (1 - \theta) P$$

where k_a is rate constant for the adsorption process.

At equilibrium the rate of desorption is equal to the rate of adsorption. That is,

$$k_d \theta = k_a (1 - \theta) P$$

$$\theta = \frac{k_a P}{K_a + k_a P}$$

$$\theta = \frac{(k_a / k_d) P}{1 + (K_a / k_d) P}$$

$$\theta = \frac{K P}{1 + K P}$$

Where K is the equilibrium constant and is referred to as the adsorption coefficient.

The amount of the gas adsorbed per gram of the adsorbent, x , is proportional to θ . Hence,



$$x \propto \frac{KP}{1 + KP}$$

$$x = K' \frac{KP}{1 + KP} \quad \dots(1)$$

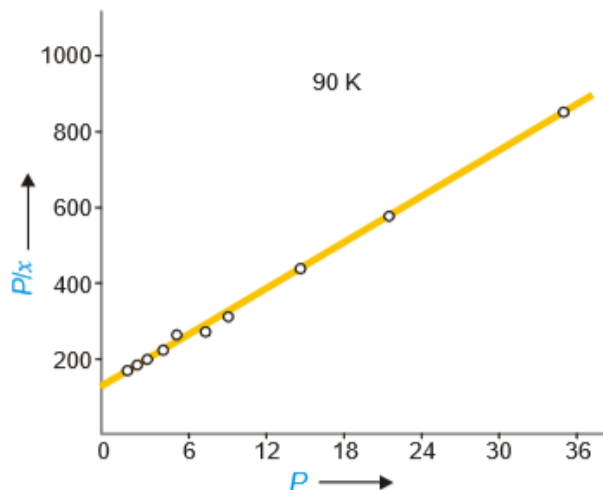
where K' is a new constant. Equation (1) gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as **Langmuir Adsorption isotherm**.

In order to test the Langmuir isotherm, equation (1) is rearranged so that

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''} \quad \dots(2)$$

where K'' constant = K'/K .

The equation (2) is similar to an equation for a straight line. Thus if P/x is plotted against P , we should get a straight line with slope $1/K''$ and the intercept $1/K'$. It was found in most cases that the actual curves were straight lines. Thus Langmuir isotherm stood verified.



Langmuir Isotherm holds at low pressures but fails at high pressures

As stated above, Langmuir Adsorption isotherm may be written as

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}$$

If the pressure (P) is very low, the factor P/K'' may be ignored and the isotherm assumes the form

$$x = K' P \text{ (at low pressure)}$$

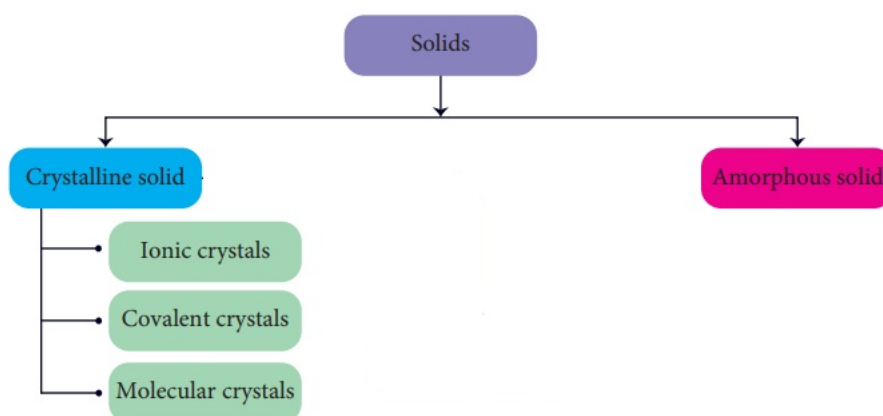


If the pressure (P) is very high, the factor $1/K'$ may be ignored and the isotherm becomes

$$x = K'' \text{ (at high pressure)}$$

Hence, at low pressures, the amount of gas adsorbed (x) is directly proportional to pressure (P). At high pressures the mass adsorbed reaches a constant value K'' when the adsorbent surface is completely covered with a unimolecular layer of the gas. At this stage adsorption is independent of pressure.

SOLID STATE



Classification of crystalline solids:

1. IONIC SOLIDS:

The structural units of an ionic crystal are cations and anions. They are bound together by strong electrostatic attractive forces. To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa. Ionic crystals possess definite crystal structure; many solids are cubic close packed. Example: The arrangement of Na^+ and Cl^- ions in NaCl crystal.

Characteristics:

1. Ionic solids have high melting points.
2. These solids do not conduct electricity, because the ions are fixed in their lattice positions.
3. They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.
4. They are hard as only strong external force can change the relative positions of ions.

2. COVALENT SOLIDS:



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DOCUMENT TITLE
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DOCUMENT NO. : **DCG 013**
REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 19 to 37

Edition : 1

In covalent solids, the constituents (atoms) are bound together in a three dimensional network entirely by covalent bonds. Examples: Diamond, silicon carbide etc. Such covalent network crystals are very hard, and have high melting point. They are usually poor thermal and electrical conductors.

3. MOLECULAR SOLIDS:

In molecular solids, the constituents are neutral molecules. They are held together by weak van der Waals forces. Generally molecular solids are soft and they do not conduct electricity. These molecular solids are further classified into three types.

(i) In non polar molecular solids:

The constituent molecules are held together by weak dispersion forces or London forces. They have low melting points and are usually in liquids or gaseous state at room temperature. Examples: naphthalene, anthracene etc.,

(ii) Polar molecular solids:

The constituents are molecules formed by polar covalent bonds. They are held together by relatively strong dipole-dipole interactions. They have higher melting points than the nonpolar molecular solids. Examples are solid CO₂ , solid NH₃ etc.

(iii) Hydrogen bonded molecular solids:

The constituents are held together by hydrogen bonds. They are generally soft solids under room temperature. Examples: solid ice (H₂ O), glucose, urea etc.,

4. METALLIC SOLIDS:

In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space. They are hard, and have high melting point. Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre. Examples: Metals and metal alloys belong to this type of solids, for example Cu, Fe, Zn, Ag ,Au, etc.

CLASSIFICATION OF CRYSTALS ON THE BASIS OF BONDS

Crystals can also be classified on the basis of the bonds that hold the ions, molecules or atoms together in the crystal lattice. Thus we have:

- (a) Ionic crystals
- (b) Molecular crystals
- (c) Network covalent crystals
- (d) Metallic crystals

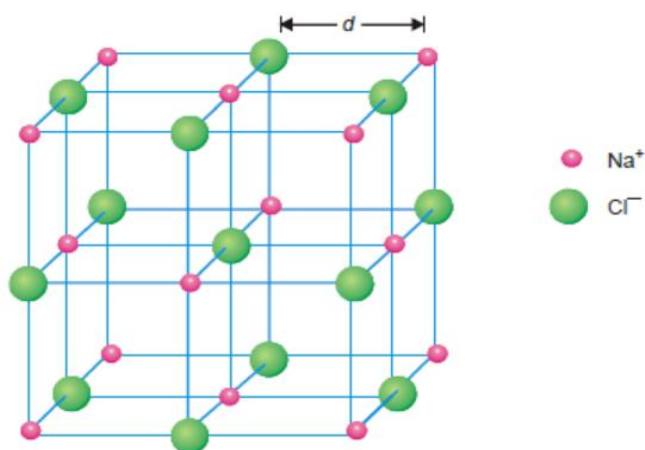
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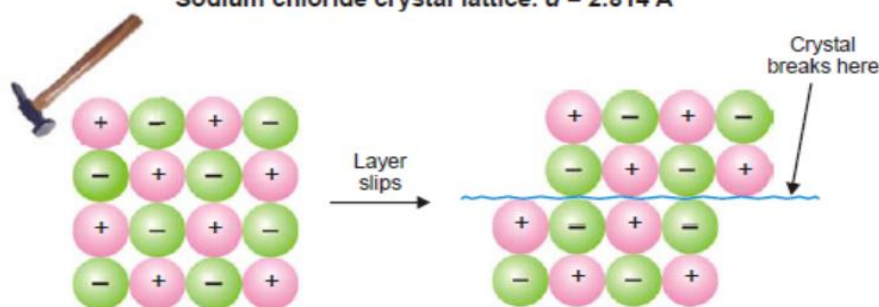


IONIC CRYSTALS

In an ionic crystal the lattice is made of positive and negative ions. These are held together by ionic bonds – the strong electrostatic attractions between oppositely charged ions. Consequently, the cations and anions attract one another and pack together in an arrangement so that the attractive forces maximize. The sodium chloride lattice shown in Figure is an example. Each ion is surrounded by neighbours of opposite charge and there are no separate molecules. Since the ions are fixed in their lattice sites, typical ionic solids are hard and rigid with high melting points. In spite of their hardness, ionic solids are brittle. They shatter easily by hammering. By hammering, a layer of ions slips away from their oppositely charged neighbours and brings them closer to ions of like charge. The increase of electrostatic repulsions along the displaced plane causes the crystal to break.



Sodium chloride crystal lattice. $d = 2.814 \text{ \AA}$



Ionic solids are non-conducting because the ions are in fixed positions. However, in the fused state the ions are allowed freedom of movement so that it becomes possible for them to conduct electricity.



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DOCUMENT NO. : **DCG 013**
REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 19 to 37

Edition : 1

MOLECULAR CRYSTALS

- In molecular crystals, molecules are the structural units. They are directional.
- These are held together by van der Waals' forces.
- When this type of crystal melts, it is only the weak van der Waals forces which can be easily disturbed. Therefore molecular solids have low melting points.
- Most organic substances are molecular solids.
- Dry ice, or frozen carbon dioxide, is the best example of molecular solid.

COVALENT CRYSTALS

- In this type of crystals atoms occupy the lattice sites.
- These atoms are bonded to one another by covalent bonds.
- The atoms interlocked by a network of covalent bonds produce a crystal which is considered to be a single giant molecule. Such a solid is called a **network covalent solid** or simply **covalent solid**.
- Since the atoms are bound by strong covalent bonds, these crystals are very hard and have very high melting points.

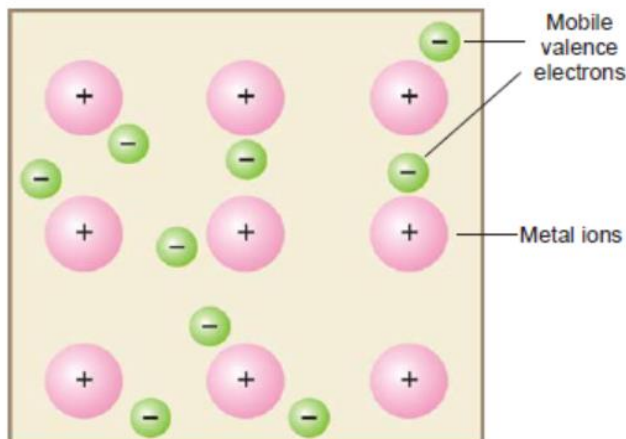
METALLIC CRYSTALS

- The crystals of metals consist of atoms present at the lattice sites.
- The atoms are arranged in different patterns, often in layers placed one above the other.
- The atoms in a metal crystal are viewed to be held together by a metallic bond.
- The valence electrons of the metal atoms are considered to be delocalized leaving positive metal ions.
- The freed electrons move throughout the vacant spaces between the ions. The electrostatic attractions between the metal ions and the electron cloud constitute the metallic bond.

Thus a metal crystal may be described as having positive ions at the lattice positions surrounded by mobile electrons throughout the crystal. The attractive force between ions and the electron cloud remains the same. The crystal, therefore, does not break.

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A representation of a metallic crystal structure.

CRYSTAL DEFECTS

So far in our discussion of crystalline substances, we have assumed them to be **perfect crystals**. A perfect crystal is one in which all the atoms or ions are lined up in a precise geometric pattern. But crystals are never actually perfect. The **real crystals** that we find in nature or prepare in the laboratory always contain imperfections in the formation of the crystal lattice. These crystal defects can profoundly affect the physical and chemical properties of a solid.

The common crystal defects are:

- (a) Vacancy defect
- (b) Interstitial defect
- (c) Impurity defects

These defects pertaining to lattice sites or points are called **Point defects**.

Vacancy Defect

When a crystal site is rendered vacant by removal of a structural unit in the lattice, the defect is referred to as the **vacancy defect**. In an ionic crystal, a cation and anion may leave the lattice to cause two vacancies. Such a defect which involves a cation and an anion vacancy in the crystal lattice is called a **Schottky defect**. This defect is found in the crystals of sodium chloride and cesium chloride (CsCl).

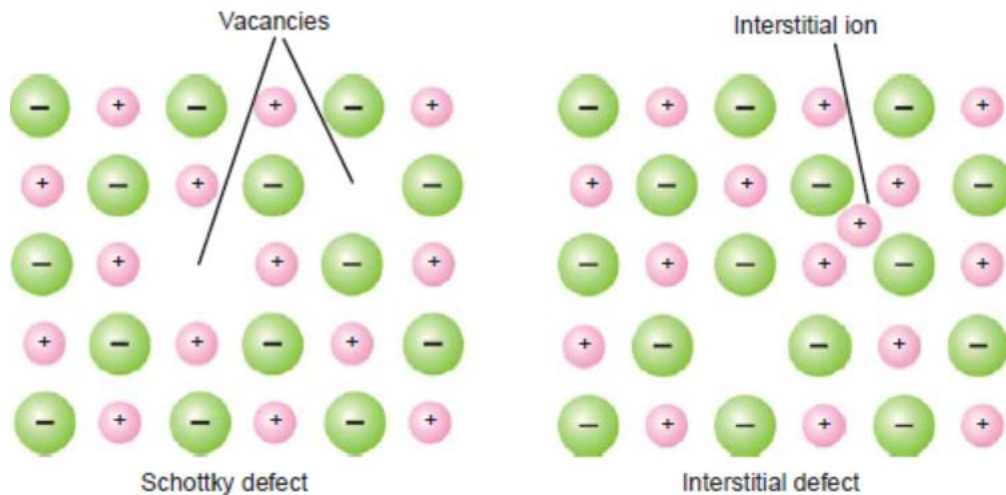
Interstitial Defect



Here, an ion leaves its regular site to occupy a position in the space between the lattice sites (interstitial position). This causes a defect known as **Interstitial defect or Frenkel defect**. As shown in Figure ordinarily the cation moves as it is smaller than the anion and can easily fit into the vacant spaces in the lattice. Thus in AgCl crystal, Ag⁺ ion occupies an interstitial position leaving a vacancy (or hole) at the original site.

Impurity Defect

These defects arise due to the corporation of foreign atoms or ions in regular lattice sites or interstitial sites. When foreign particles are substituted for normal lattice particles, it is called **substitution impurity**.



When foreign particles are trapped in vacant interstitial spaces, it is called **interstitial impurity**. Both types of impurities can have drastic effect on the properties of solids.

Stoichiometric defects in ionic solid:

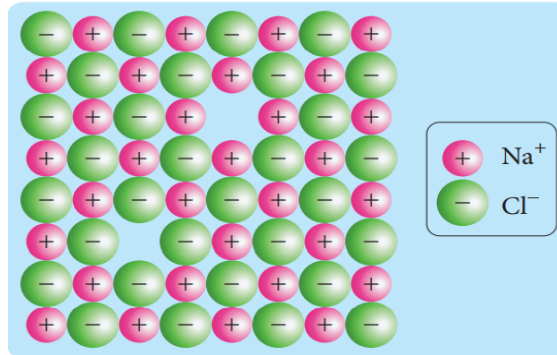
This defect is also called intrinsic (or) thermodynamic defect. In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

(a) Schottky defect:

Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice. This effect does not change the Stoichiometry of the crystal. Ionic solids in which the



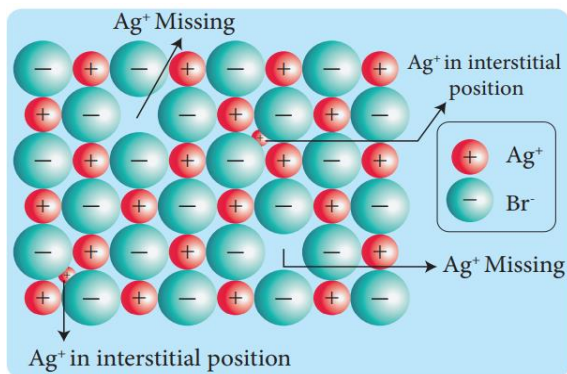
cation and anion are of almost of similar size show Schottky defect. Example: NaCl. Presence of large number of Schottky defects in a crystal, lowers its density.



Schottky Defect

(b) Frenkel defect:

Frenkel defect arises due to the dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position. This defect is shown by ionic solids in which cation and anion differ in size. Unlike Schottky defect, this defect does not affect the density of the crystal. For example AgBr, in this case, small Ag⁺ ion leaves its normal site and occupies an interstitial position as shown in the figure.



Frenkel Defect

CONDUCTORS

Those substances which allow electrical current to pass through them completely are known as conductors. Examples are metals, alloys and fused electrovalent compounds.

Applications of Conductors

Conductors are quite useful in many ways. They find use in many real-life applications. For example,



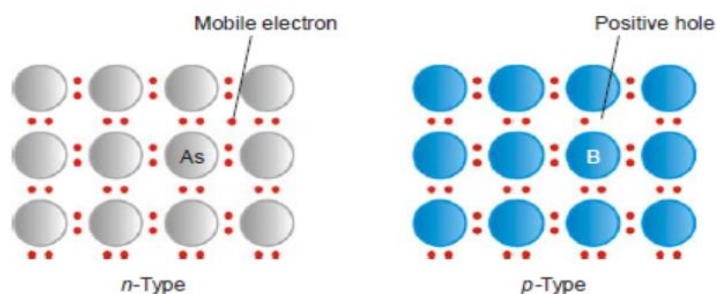
- Mercury is a common material in thermometer to check the temperature of the body.
- Aluminium finds its use in making foils to store food. It is also used in the production of fry pans to store heat quickly.
- Iron is a common material used in vehicle engine manufacturing to conduct heat.
- The plate of iron is made up of steel to absorb heat briskly.
- Conductors find their use in car radiators to eradicate heat away from the engine.

SEMICONDUCTORS

Typical metals are good conductors of electricity while elements like silicon and germanium are non conductors at ordinary temperature. However, they exhibit appreciable conductivity upon addition of impurities as arsenic and boron. The resulting materials are called **semiconductors** (poor conductors). The increase of conductivity upon addition of arsenic and boron can be easily explained.

In silicon and germanium crystals, each atom is covalently bonded to four neighbours so that all its four valence electrons are tied down. Thus in the pure state these elements are nonconductors. Suppose an atom of arsenic is introduced in place of silicon or germanium in the crystal lattice.

Arsenic has five valence electrons, four of which will be utilized in the formation of covalent bonds and the remaining electron is free to move through the lattice. This leads to enhanced conductivity.



Semiconductors derived from Silicon. n-Type semiconductor has As atom impurity and a mobile electron; p-Type conductor has B atom and positive hole.

Now let a boron atom be introduced in place of silicon atom in the crystal lattice. A boron atom has only three valence electrons. It can form only three of the four bonds required for a perfect lattice. Thus it is surrounded by seven electrons (one of Si) rather than eight. In this sense, there is produced an electron vacancy or a 'positive hole' in the lattice. Another electron from the bond of the adjacent Si



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PAGE 19 to 37

Edition : 1

atom moves into this hole, completing the four bonds on the *B* atom. This electron also leaves a hole at its original site. In this way electrons move from atom to atom through the crystal structure and the holes move in the opposite direction. Therefore the conductivity of the material improves.

- Semiconductors which exhibit conductivity due to the flow of excess negative electrons are called ***n*-type semiconductors** (*n* for negative).
- Semiconductors which exhibit conductivity due to the positive holes are called ***p*-type semiconductors** (*p* for positive).

Applications of Semiconductors:

Their reliability, compactness, low cost and controlled conduction of electricity make them ideal to be used for various purposes in a wide range of components and devices. Transistors, diodes, photo sensors, rectifiers microcontrollers, integrated chips, solar cells and much more are made up of semiconductors.

Uses of Semiconductors in Everyday life

- Temperature sensors are made with semiconductor devices.
- They are used in 3D printing machines
- Used in microchips and self-driving cars
- Used in calculators, solar plates, computers and other electronic devices.
- Transistor and MOSFET (metal–oxide–semiconductor field-effect transistor) used as a switch in Electrical Circuits are manufactured using the semiconductors.

Industrial Uses of Semiconductors:

The physical and chemical properties of semiconductors make them capable of designing technological wonders like microchips, transistors, LEDs, solar cells, etc. The microprocessor used for controlling the operation of space vehicles, trains, robots, etc is made up of transistors and other controlling devices which are manufactured by semiconductor materials.

Insulators

Insulators are the materials or substances which resist or don't allow the current to flow through them. In general, they are solid in nature. Also, insulators are finding use in a variety of systems. As they

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DATE : **05/04/2021**
COPY :
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Edition : 1

do not allow the flow of heat. The property which makes insulators different from conductors is its resistivity.

Wood, cloth, glass, mica, and quartz are some good examples of insulators. Also, insulators are protectors. They give protection against heat, sound and of course passage of electricity. Furthermore, insulators don't have any free electrons. It is the main reason why they don't conduct electricity.

Applications of Insulators

As insulators resist the flow of electron, they find worldwide applications. Some of the common uses include:

- Thermal insulators, disallow heat to move from one place to another. Hence, we use them in making thermoplastic bottles. They are also used in fireproofing ceilings and walls.
- Sound insulators help in controlling noise level, as they are good in absorbance of sound. Thus, we use them in buildings and conference halls to make them noise-free.
- Electrical insulators hinder the flow of electron or passage of current through them. So, we use them extensively in circuit boards and high-voltage systems. They are also used in coating electric wire and cables.

Band Theory of Solids

This theory explains the quantum state that an electron takes inside metal solid. Every molecule comprises of various discrete energy levels. The way electrons behave inside a molecule is well explained through this theory.

- In atoms, electrons are filled in respective energy orbits following Pauli's exclusion principle.
- In molecules, two atomic orbitals combine together to form a molecular orbit with two distinct energy levels.
- In solids, 10^{23} stacked up lines confined in a tiny space would look like a band. Thereby forming energy continuum called energy bands.
- This theory helps to visualise the difference between conductor, semiconductor and an insulator by plotting available energies for an electron in a material.

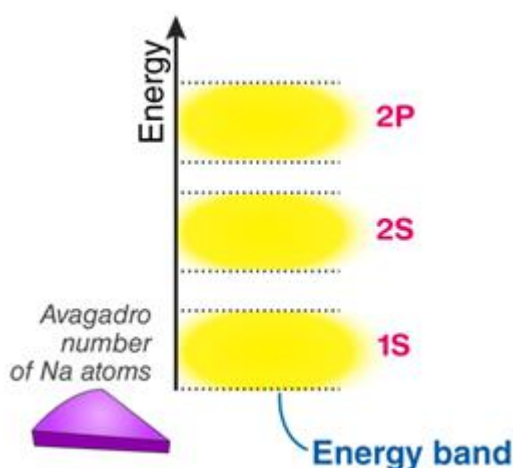
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Energy levels inside a solid made up of n-number of atoms

In general, if there is n-number of atoms, then there will be n discrete energy levels in each energy band. In such a system of n number of atoms, the molecular orbital's are called as energy bands. Single 1s orbital and 2s orbital can fit 2 electrons each. Thus, the total number of electrons a 1s and 2s energy band can fit is 2n. A single 2p level can fit 6 electrons so 2p energy band can fit is 6n electron so on and so forth.



The band theory of solids is different from the others because the atoms are arranged very close to each other such that the energy levels of the outermost orbital electrons are affected. But the energy level of the innermost electrons is not affected by the neighbouring atoms.

In band theory of solid, there are many energy bands but the following are the three most important energy bands in solids:

1. Valence band
2. Conduction band
3. Forbidden band

Valence band:

The energy band that consists of valence electrons energy levels is known as the valence band. The valence band is present below the conduction band and the electrons of this band are loosely bound to the nucleus of the atom.



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REV. NO. : **R0**
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COPY :
PAGE 19 to 37

Edition : 1

Conduction band:

The energy band that consists of free electrons energy levels is known as the conduction band. For electrons to be free, external energy must be applied such that the valence electrons get pushed to the conduction band and become free.

Forbidden band:

The energy gap between the valence band and the conduction band is known as the forbidden band which is also known as the forbidden gap. The electrical conductivity of a solid is determined from the forbidden gap and also the classification of the materials as conductors, semiconductors and insulator.

A useful way to visualize the difference between [conductors](#), [insulators](#) and [semiconductors](#) is to plot the available energies for electrons in the materials. Instead of having [discrete energies](#) as in the case of free atoms, the available energy states form [bands](#). Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a [doping](#) material can increase conductivity dramatically.

An important parameter in the band theory is the [Fermi level](#), the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.

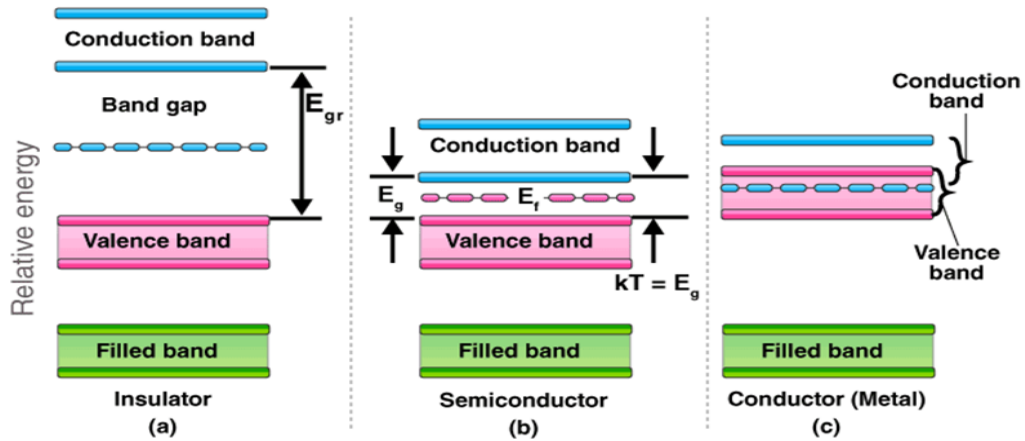
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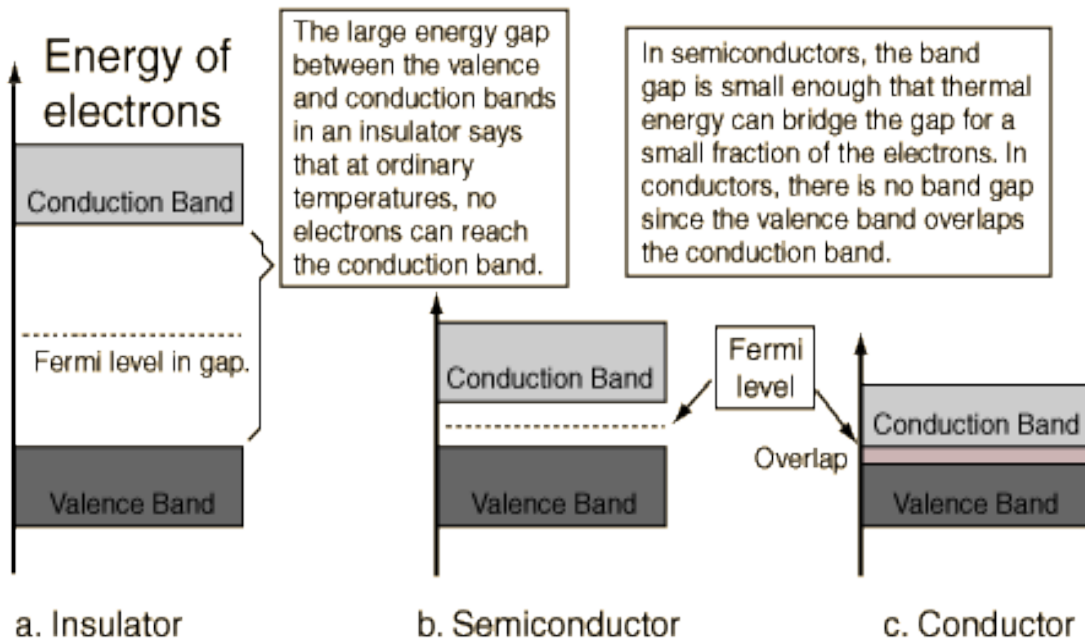
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ENERGY BAND GAPS IN MATERIALS



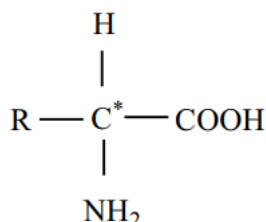
Energy Band Diagram for Semiconductors, Conductors, and Insulators





Amino acids:

Amino acids are compounds which contain an amino group and a carboxylic acid group. The protein molecules are made up α -amino acids which can be represented by the following general formula.

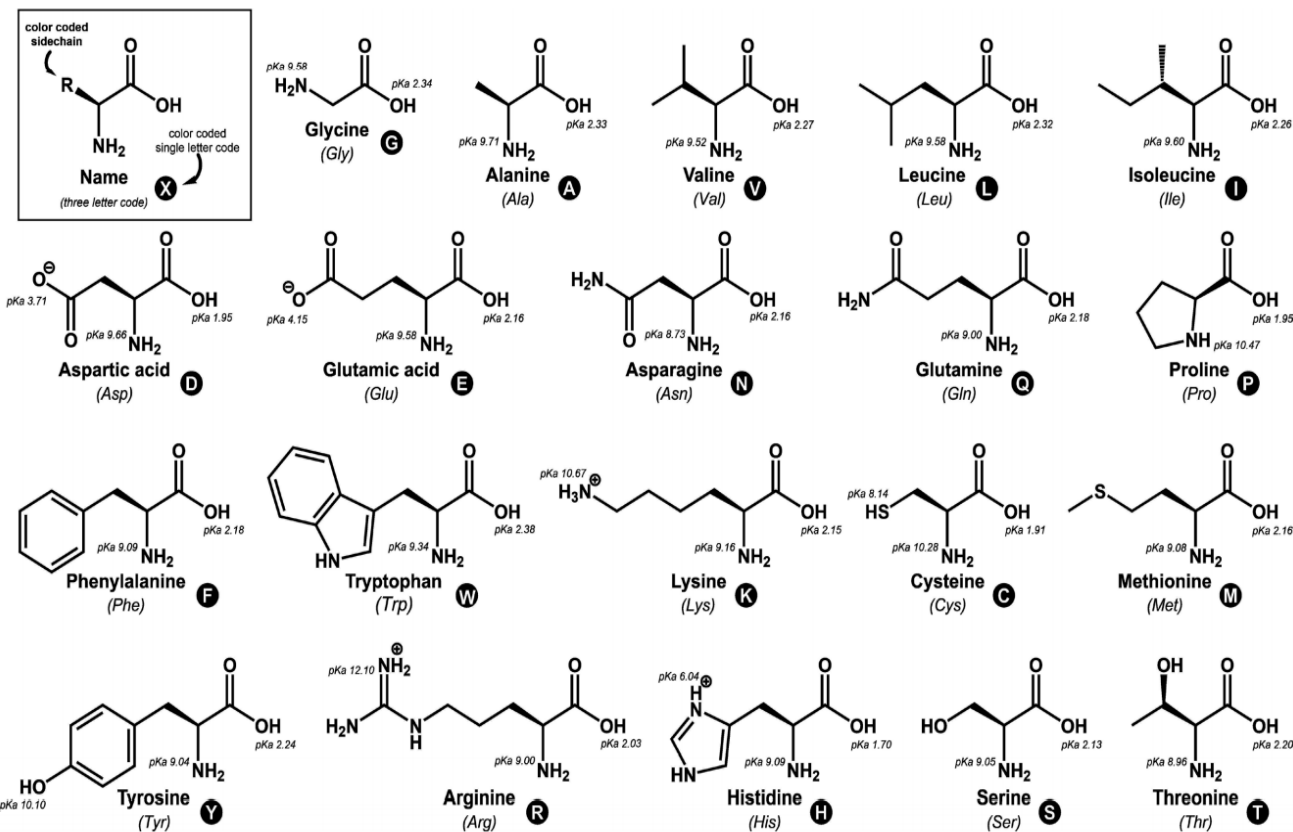


R group varies in structure, size, electric charge and influence the solubility of amino acid in water.

The key elements of amino acids are C, N, O, and H. Amino acids are basic structural building blocks of protein.

There are 20 α -amino acids commonly found in the protein molecules. Each amino acid is given a trivial name, a three letter code and a one letter code. In writing the amino acid sequence of a protein, generally either one letter or three letter codes are used.

AMINO ACIDS AND THEIR STRUCTURE





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REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 38 OF 62

Edition : 1

Classification of amino acids

I Classification based on biological importance

- (i) Essential amino acid: certain amino acid that cannot be synthesis by living organism. They must be compulsorily included in the diet. Eg.Valine, theronine etc.
- (ii) Non-essential amino acid: Certain amino acid that can be synthesised by the cell . They need not included in diet. Eg: Alanine, Glycine etc.

II Classification based on incorporation in protein:

- (i) Proteogenic Amino acid: It is used for synthesis of protein Eg: Hydroxyproline
- (ii) Non-Proteogenic amino acid: It is not used for synthesis of protein. Eg: β -Alanine

III Classification based on structure of side chain:

- (i) Aliphatic amino acid: They are long chain molecule
- (ii) Aromatic amino acid: They contain benzene ring

IV Classification based on position of $-NH_2$ group

- (i) α -Amino acid
- (ii) β -Amino acid
- (iii) β -Amino propionic acid
- (iv) γ - Amino acid

V Classification based on reaction in solution

- (i) Neutral : Eg: Tryosine
- (ii) Acidic : Eg: Asparagine
- (iii) Basic : Eg: Histidine

VI Classification based on Polarity of side chain:

- (i) Hydrophobic : Alanine
- (ii) Hydrophilic : Glycine

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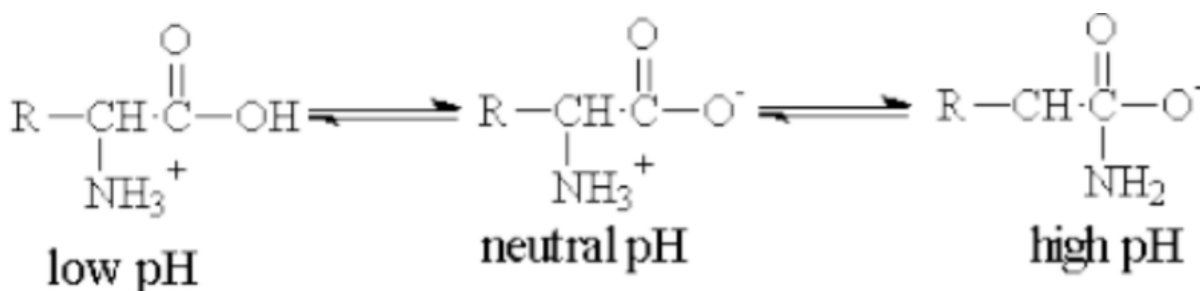


Preparation of amino acids:

Properties of amino acid:

Amino acids are colourless, water soluble crystalline solids. Since they have both carboxyl group and amino group their properties differ from regular amines and carboxylic acids.

1- Amphoteric Compounds: which mean they can act as acids and bases, due to presence of carboxyl group COOH that able to donate proton(H⁺), and convert to COO⁻ also presence of amino group NH₂ which is enable to accept this proton(H⁺) and convert into NH₃⁺

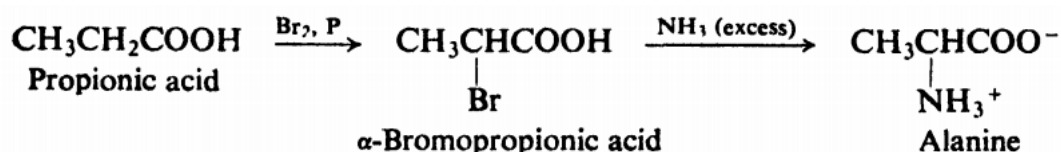


2. Iso electric point (PI) : It is the pH value at which concentration of anionic and cationic groups are equal (i.e. the net charge of this molecule equals zero) It is known as a point at which the molecule does not move to either cathode or anode if it is put in electric field and its solubility is minimum so it is possible to precipitate at this point. Each amino acid have a different PI

3-Rotate the polarized light Amino acids are able to rotate polarized light either to the left (livo) L- a.a or to the right (dextro) D- a.a , since they have an asymmetric C atom (a carbon atom linked to 4 different groups), except glycine which lacks asymmetric C atom (has 2 H+ on α-C) .

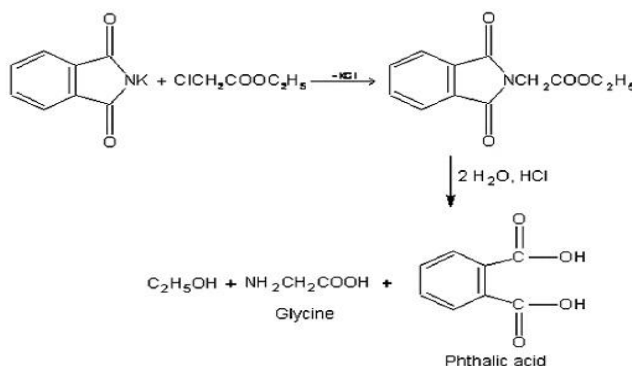
Preparation of amino acids:

- (i) An α-chloro or α -bromo acid is subjected to direct ammonolysis with a large excess of concentrated aqueous ammonia. For example:





(ii) Preparation of amino acid from Potassium phthalimide with chlormethylethonate gives glycine.



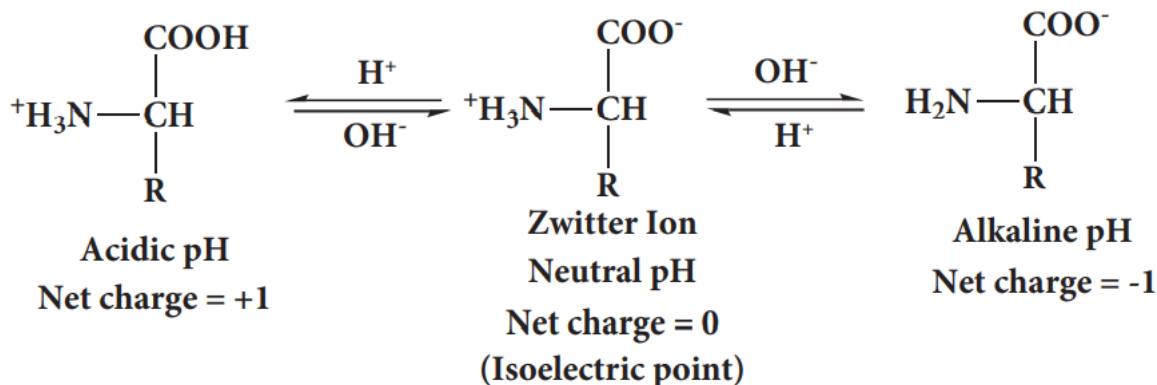
Isoelectric point: (PI)

It is the pH value at which concentration of anionic and cationic groups are equal (i.e. the net charge of this molecule equals zero) It is known as a point at which the molecule does not move to either cathode or anode if it is put in electric field and its solubility is minimum so it is possible to precipitate at this point. Each amino acid has a different PI

The carboxyl group can lose a proton and become negatively charged or the amino group can accept a proton to become positively charged depending upon the pH of the solution. At a specific pH the net charge of an amino acid is neutral and this pH is called isoelectric point. At a pH above the isoelectric point the amino acid will be negatively charged and positively charged at pH values below the isoelectric point.

Zwitter ions:

In aqueous solution the proton from carboxyl group can be transferred to the amino group of an amino acid leaving these groups with opposite charges. Despite having both positive and negative charges this molecule is neutral and has amphoteric behaviour. These ions are called zwitter ions.





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REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 38 OF 62

Edition : 1

4. The formation of black precipitate at the bottom of the test tube. This indicates the presence of cysteine or cystine in the solution.

III Millon's Test

1. About 2 ml of the sample solution or the 1% tyrosine solution is taken in a test tube.
2. To this, about 2 ml of Millon's reagent is added. The test tubes are then kept in the water bath for about 2 minutes if red colored precipitate is not observed immediately.
3. The tubes are then observed for the formation of the colored precipitate.
4. The formation of a red or pink colored precipitate. This indicates the presence of tyrosine or tyrosine containing protein.

IV Xanthoproteic Test:

1. About 1 ml of the sample solution is taken in a test tube. To this, the same amount of concentrated nitric acid is added.
2. The test tube is allowed to cool down to room temperature. If the sample is a protein solution, a white precipitate might develop due to the denaturation of proteins.
3. Then, 1 ml of 40% NaOH solution is added to the test tube and observed for color change.
4. The appearance of a dark yellow or orange-colored solution represents a positive test. This indicates the presence of aromatic groups in the proteins and amino acids.

V Isatin test:

1. A drop of the sample (imino acid) solution is added to a Whatman No. 1 filter paper and dried by placing it in a hot air oven.
2. Now, a drop of isatin reagent is added to the dried spot, and the process of drying in the hot air oven is repeated.
3. The paper is then observed for the formation of a blue-colored spot.
4. The formation of a blue-colored spot on the filter paper. This indicates the presence of imino acids.

PROTEINS

Proteins are a macromolecule composed of one or more polypeptide chains possessing a characteristic amino acid sequence. It is a polymer of amino acids.

Classification of Proteins:

Proteins are classified in two ways.

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- (i) On the basis of their solubility or shape
- (ii) On the basis of increasing complexity of structure

I Classification of proteins on the basis of solubility or shape:

Proteins are classified in two groups based on their solubility and shape. They are globular proteins and fibrous proteins.

1. Globular proteins: Globular proteins are spherical in shape and are soluble in water. They are highly branched. The polypeptide chain are cross linked by the usual peptide bonds involving the second amino group of one amino acid and the second carboxyl group of the second amino acid. The globular protein molecules may also be tightly folded into spherical or globular shapes. The globular proteins include (a) Enzymes (b) Protein hormones (c) Antibodies (d) Blood proteins such as haemoglobins, myoglobin, immunoglobulin and insulin.
2. Fibrous Proteins: Fibrous are insoluble in water. These are highly resistant to digestion by proteolytic enzymes. They are unbranched and are in the form of fibres. They are linear molecule. The long linear protein chains are held together by intermolecular hydrogen bonds. They are not folded into globular molecules. They serve as structural proteins.

II Classification of proteins based on the increasing complexity of structure:

On the basis of increasing complexity of structure, proteins are classified into three groups. They are:

- (a) Simple proteins
- (b) Conjugated proteins
- (c) Derived proteins

(A)SIMPLE PROTEINS:

The proteins which yield amino acids or their derivatives on hydrolysis are called simple proteins. Simple proteins are further classified into 7 sub class on the basis of the decreasing solubility.

- (i) Albumins:
Albumins are simple proteins soluble in water. They are coagulated by heat. They are precipitated by saturated ammonium sulphate salt solution. They are deficient in glycine. Eg. Plasma albumin, serum albumin of egg, ovalbumin of egg, white lactalbumin of milk.
- (ii) Globulins:



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DOCUMENT NO. : **DCG 014**
REV. NO. : **R0**
DATE : **05/04/2021**
COPY :
PAGE 38 OF 62

Edition : 1

Globulins are insoluble in water, but soluble in dilute solutions of neutral salts. They are coagulated by heat. They are precipitated by lower concentration of salts such as ammonium sulphate or sodium sulphate. Globulins are precipitated by saturated NaCl solution. They contain glycine. Eg. Plasma globulin, serum globulin, ovaglobulin in egg white, mosin in muscles, and edestin in hemp seed.

- (iii) Gluteline: Gluteline are insoluble in water and dilute solutions of neutral salts. But they are soluble in acids and bases. They are acid. Eg. Glutenin in whet oryzenin in rice.
- (iv) Prolamines: Prolamines are soluble in 70 to 80 % ethyl alcohol. But they are insoluble in waer, absolute alcohol and other neutral solvents. They are not coagulated by heat. They contain large amount of protein. They are deficient of lysine. Eg. Zein from maize, gliadin from wheat, ordain from barley and secalin from rye.
- (v) Albuminiods: these proteins are insoluble in water, dilute solutions of neutral salts, acid bases and 60 to 80 % ethyl alcohol. But they are soluble in long boiling concentrated acid solutions. Eg. Keratin in hair, feathers, nails, etc.
- (vi) Histones: Histones are simple proteins soluble in water and dilute acids, but insoluble in ammonia. They are not coagulated by heat. Histones are rich in basic amino acids like histidine and arginine but deficient in tryptophan and contain little cystine or methonine. Histones are combined with nucleic acids and haemoglobin.
- (vii) Protamines: Protamines are soluble in water and ammonium hydroxide. They are not coagulated by hest. They are more basic than histones. They contain large quantities of arginine. Tyrosine and tryptophan are absent. Eg. Salamine etc.

(B) CONJUGATED PROTEINS:

Conjugated proteins are proteins united with non-protein substances. The non-protein substance linked to proteins is referred to as prosthetic group. So conjugated proteins, on hydrolysis, yield non-proteon substances in addition to amino acids. The conjugate proteins are further classified into 5 sub types.

- (i) Glycoproteins or Mucoproteins: Glycoproteins contains carbohydrates as the prosthetic group. On hydrolysis they yield amino sugars. Eg. Mucin in saliva, egg, albumin etc.

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- (ii) Phosphoproteins: Phosphoproteins contain phosphoric acid the prosthetic group. The phosphoric acid is attached to the hydroxyl group of protein by an ester linkage. Eg. Casein in milk, vitellin in egg yolk.
- (iii) Lipoproteins: It contains phospholipids cholesterol as the prosthetic group, Eg. Lipoproteins of blood serum.
- (iv) Nucleoproteins: These contain nucleic acid as the prosthetic group. Eg. Nuclein, nucleohistone etc.
- (v) Chromo proteins: Chromo proteins are coloured proteins. These are simple proteins linked to a metallic prosthetic group which gives the colour to the protein. Eg. Haemoglobin, haemocyan chlorophyll etc.

(C) DERIVED PROTEINS:

Derived proteins are the intermediate products formed from natural proteins when they are hydrolysed by heat, acids, alkalis enzymes,. The derived proteins are of two types. They are primary proteins and secondary proteins.

I PRIMARY DERIVED PROTEINS:

- (i) Proteans: proteans are denatured proteins. They are the fibre products produced by the action of acids, enzymes or water proteins. They are insoluble in water. Eg. a) edestan from edestin b) fibrin from fibrinogen c) myosin derived from myosin.
- (ii) Metaproteins: These are derived by the further action of acid or alkali on proteins. These are insoluble in water, but soluble in dilute acid or alkali.
- (iii) Coagulated proteins: these are insoluble protein products produced by the action of heat or alcohol on protein coagulated egg white is an example of this type.

II SECONDARY DERIVED PROTEINS:

Secondary derived proteins are the products of proteins in which definite hydrolysis has taken place. The molecules are smaller than those of the original protein. They may be mainly of three types, namely proteases, peptones, polypeptides.

- (i) Proteases: It is insoluble in water. They are not coagulated by heat. They are precipitated by saturating their solutions with ammonium sulphate.



- (ii) Peptones: it is soluble in water. They are not coagulated by heat. They are also not precipitated by saturating their solution with ammonium sulphate.
- (iii) Polypeptides: These are the derivatives of proteins containing amino acids units.

STRUCTURE OF PROTEINS:

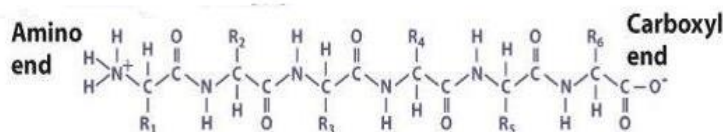
Different structural organisation for proteins. They are.

1. Primary structure
2. Secondary structure
3. Tertiary structure
4. Quaternary structure

I PRIMARY STRUCTURE:

The primary structure of protein is defined as the linear sequence amino acid residues up its polypeptide chain. The protein nor formed of one or more polypeptide chains. The amino acids arranged in specific sequence in the polypeptide chain. The peptide bond is a repeating unit. Two amino acids give dipeptide, three amino acids give a tripeptide, four amino acid gives tetra-peptide and so on. More than 10 amino acids form a polypeptide. Polypeptide has a) N-terminal b) C-terminal .The primary structure has salient features:

1. Primary structure refers to the linear sequence of amino residues.
2. The proteins are linear and unfolded.
3. The protein is formed of one or more polypeptide chains.
4. The amino acid residues are linked by repeating peptide bond
5. The adjacent polypeptide chains are linked by disulphide bond.
6. Most of the structural proteins which are in the form of for exhibit primary structure. Eg: Fibrous of silk.

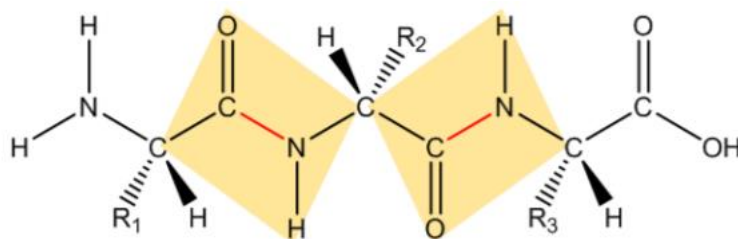


[Figure 1 : The sequence of a polypeptide chain from an antibody, with the N- and the C-termininal]



II SECONDARY STRUCTURE:

The peptide bond between two residues is a single bond, but it is said to have a semi double-bond character. This means that it is particularly rigid for a single bond, forming a planar structure called the amide plane, as shown in Figure 2.



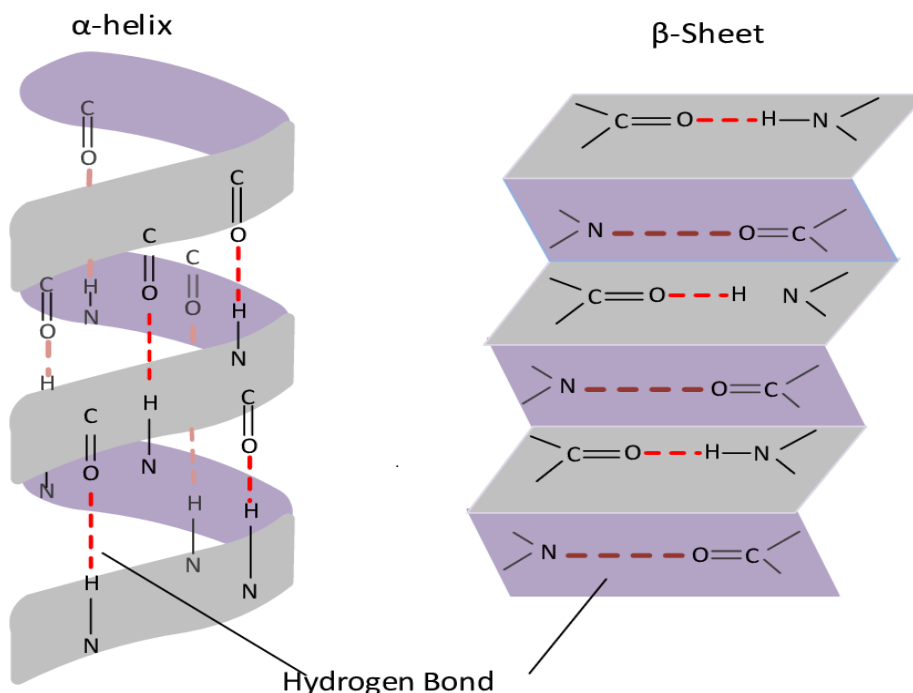
[Figure 2 | The amide planes of a tripeptide. Each peptide bond (red) forms a planar structure, the amide plane (yellow), due to its semi double-bond character. R1-3: side chains.]

The angles between subsequent amide planes in a polypeptide are called torsion angles. They can only adopt certain values, and those values impose certain conformations (or folds) on the backbone.

⇒ The secondary structure of a protein is the local fold of the protein backbone.

Some of those local folds form precise, regular structures, often stabilised by hydrogen bonds. The two most common examples of secondary structure elements are α -helices and β -sheets.

In an α -helix, the polypeptide chain forms a right-handed helical structure with 3.6 residues per turn (Figure 3a). The helix is stabilised by hydrogen bonds between the backbone N–H of each residue and the backbone C=O of the amino acid four residues earlier in the sequence. The core of the helix is tightly packed and all the side chains project outward.



[Figure 3a | Example of an α -helix containing alanine residues only. Hydrogen bonds (orange) between backbone atoms four residues apart stabilise the α -helix. Figure 3b | Example of a β -sheet. All side chain atoms are hidden for simplicity. Hydrogen bonds between backbone atoms from adjacent β -strands stabilise the β -sheet.]

β -sheets are the other most common type of secondary structure element, shown in Figure 3b. They are also stabilised by hydrogen bonds, but between different chains, whereas in an α -helix, the hydrogen bonds are all within the same helix. Similarly to α -helices however, the hydrogen bonds stabilising β -sheets are between backbone N-H and C=O groups.

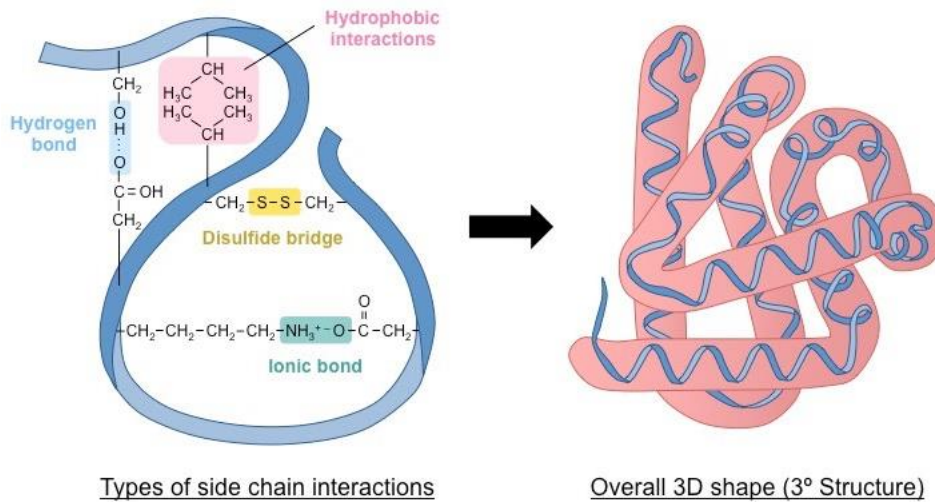
III TERTIARY STRUCTURE

⇒ The tertiary structure of a protein is its overall 3D arrangement: the folding of secondary structure elements and the position of side chains.

The hydrophobic effect is responsible for most of the tertiary structure of a protein: it is energetically favourable for the protein to fold and bury its hydrophobic residues within its core, away from the surrounding water. Other bonds and interactions also help the protein fold into the correct tertiary structure. Disulphide bonds are covalent bonds between the sulphur atoms of two cysteine residues. Salt bridges are electrostatic interactions between a negatively charged side chain and a positively charged one. Hydrogen bonds and van der Waals interactions



(between hydrophobic residues) are also involved in the tertiary structure. All those forces, interactions and bonds are shown in Figure 4.

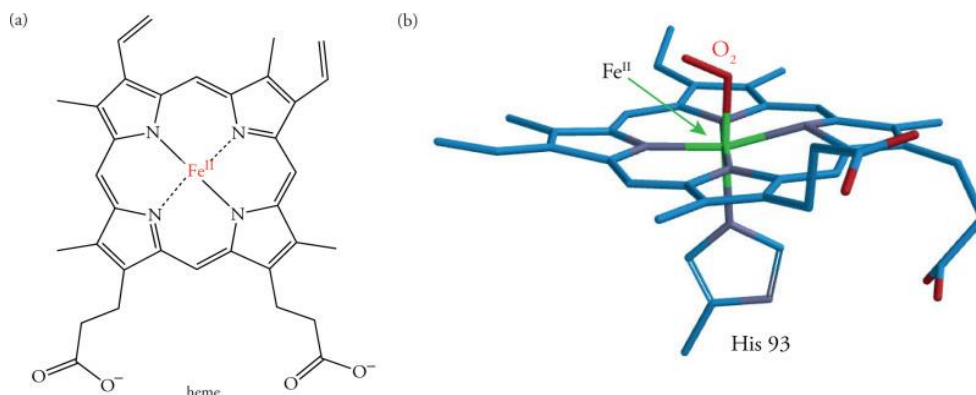


[Figure 4 | The forces, bonds and interactions responsible for protein tertiary structure]

IV QUATERNARY STRUCTURE:

Some proteins are also covalently attached to a non-protein element, e.g. the haem cofactor in haemoglobin (cf. worksheet on haemoglobin).

⇒ the quaternary structure of a protein is the assembly of several polypeptide chains, and sometimes the addition of a non-protein element, to form a functional protein.



[Figure 5 |the quaternary structure of an antibody, comprising two heavy chains and two light chains]

The same forces, bonds and interactions responsible for tertiary structure may be involved in holding different polypeptide chains together.



ENZYME CATALYSIS

Numerous organic reactions are taking place in the body of animals and plants to maintain the life process. These reactions being slow remarkably catalysed by the organic compounds known as **Enzymes**. All enzymes have been found to be complex protein molecules. Thus : Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells. **The catalysis brought about by enzymes is known as Enzyme Catalysis.**

Each enzyme is produced in a particular living cell to catalyse a reaction occurring in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However the first enzyme as prepared by synthesis in the laboratory in 1969.

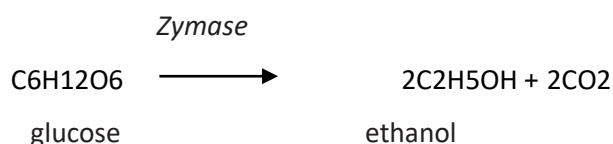
Examples of Enzyme Catalysis

Some common examples of the biochemical reactions catalysed by enzymes are :

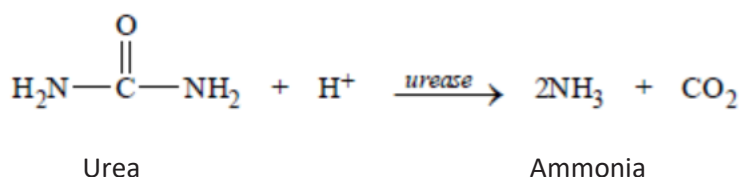
(1) **Inversion of cane sugar** ($C_{12}H_{22}O_{11}$) by *Invertase present in yeast,*



(2) **Conversion of glucose into ethanol** by *Zymase present in yeast,*



(3) **Hydrolysis of urea** ($H_2N-CO-NH_2$) by *Urease present in soya bean*

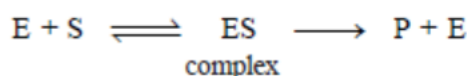




MECHANISM OF ENZYME CATALYSIS

The long chains of the enzyme (protein) molecules are coiled on each other to make a rigid colloidal particle with cavities on its surface. These cavities which are of characteristic shape and abound in active groups (NH₂, COOH, SH, OH) are termed **Active centres**. The molecules of substrate which have complementary shape, fit into these cavities just as key fits into a lock (**Lock-and- Key theory**). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the products. Thus the substrate molecules enter the cavities, forms complex and reacts, and at once the products get out of the cavities.

Michaelis and Menten (1913) proposed the following mechanism for enzyme catalysis (Fig. 6).



where E = enzyme; S = substrate (reactant); ES = activated complex; P = products.

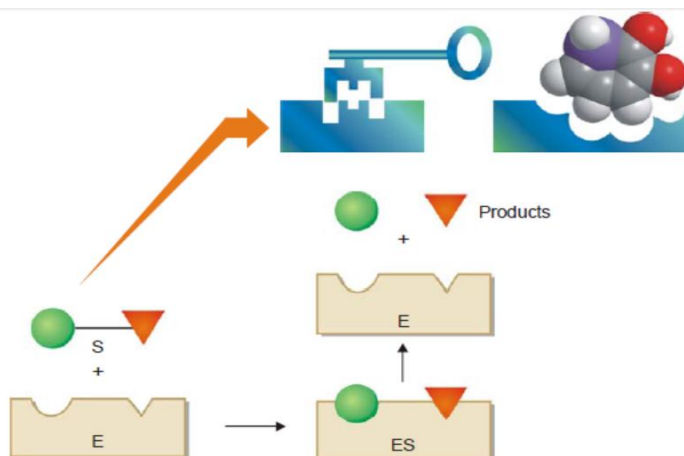


Figure:6 Illustration of the lock-and-key model of enzyme catalysis.

CHARACTERISTICS OF ENZYME CATALYSIS

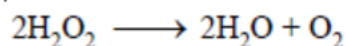
In general, enzyme behave like inorganic heterogeneous catalysts. However, they are unique in their efficiency and high degree of specificity. Some more important features of enzyme catalysis are listed below.

(1) Enzymes are the most efficient catalysts known

The enzyme catalysed reactions proceed at fantastic high rates in comparison to those catalysed by inorganic substances. Thus one molecule of an enzyme may transform one million molecules of the substrate (reactant) per minute.



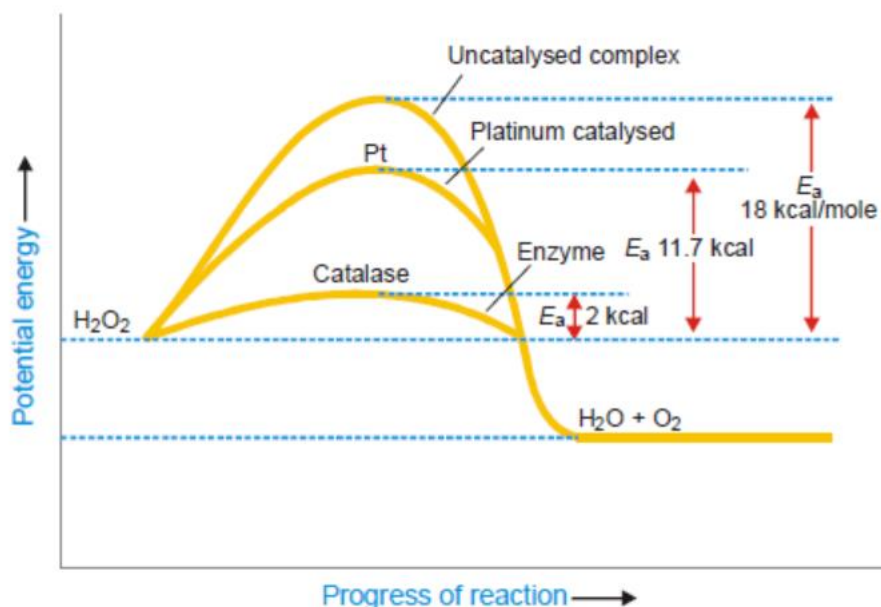
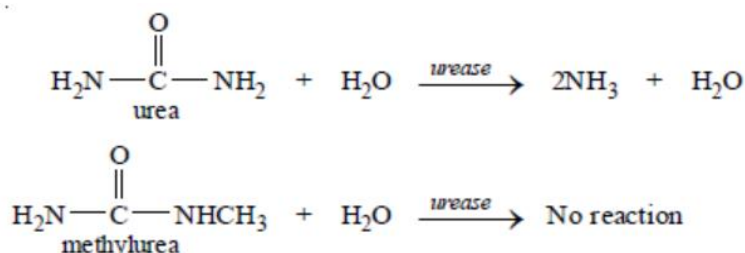
Like inorganic catalysts, enzymes function by lowering the activation energy of a reaction. For example, the activation energy of the decomposition of hydrogen peroxide,



without a catalyst is 18 kcal/mole. With colloidal platinum (inorganic catalyst), the activation energy is lowered by 11.7 kcal/mole. The enzyme *catalase* lowers the activation energy of the same reaction to less than 2 kcal/mole.

(2) Enzyme catalysis is marked by absolute specificity

An enzyme as a rule catalyses just one reaction with a particular substance. For example, *urease* (an enzyme derived from soya bean) catalyses the hydrolysis of urea and no other amide, not even methylurea.

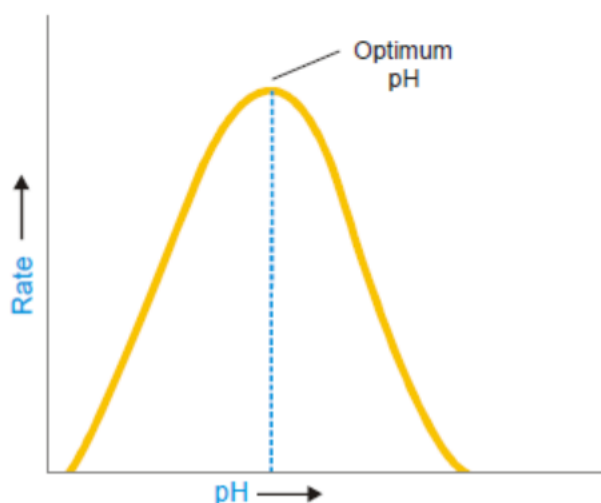


Enzyme lowers the activation energy of the decomposition of H_2O_2 by maximum which explains for their extremely high catalytic efficiency.



(3) The rate of enzyme catalyzed reactions is maximum at the optimum temperature

The rate of an enzyme catalyzed reaction is increased with the rise of temperature but up to a certain point. Thereafter the enzyme is denatured as its protein structure is gradually destroyed. Thus the rate of reaction drops and eventually becomes zero when the enzyme is completely destroyed. The rate of an enzyme reaction with raising of temperature gives a bell-shaped curve. The temperature at which the reaction rate is maximum is called the **optimum temperature**.



The variation of rate of an enzyme catalysed reaction with increase of pH.

(4) Rate of enzyme catalyzed reactions is maximum at the optimum pH

The rate of an enzyme catalyzed reaction varies with pH of the system. The rate passes through a maximum at a particular pH, known as the **optimum pH**. The enzyme activity is lower at other values of pH. Thus many enzymes of the body function best at pH of about 7.4, the pH of the blood and body fluids.

(5) Enzymes are markedly inhibited or poisoned

The catalytic activity of an enzyme is often reduced (*inhibited*) or completely destroyed (*poisoned*) by addition of other substances. These inhibitors or poisons interact with the active functional groups on the enzyme surface. For example, heavy metal ions (Ag^+ , Hg^{2+}) react with the $-\text{SH}$ groups of the enzyme and poison it.





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PAGE 38 OF 62

Edition : 1

(6) Catalytic activity of enzymes is greatly enhanced by the presence of Activators or Coenzymes

Activators are metal ions Na^+ , Mn^{2+} , CO_2^+ , Cu^{2+} , etc., which get weakly bonded to enzyme molecules and promote their catalytic action. Thus it has been found that the addition of sodium chloride (Na^+) makes *amylase* catalytically very active.

Often, a small nonprotein (*vitamin*) termed a **coenzyme** when present along with an enzyme, promotes the catalytic activity of the latter.

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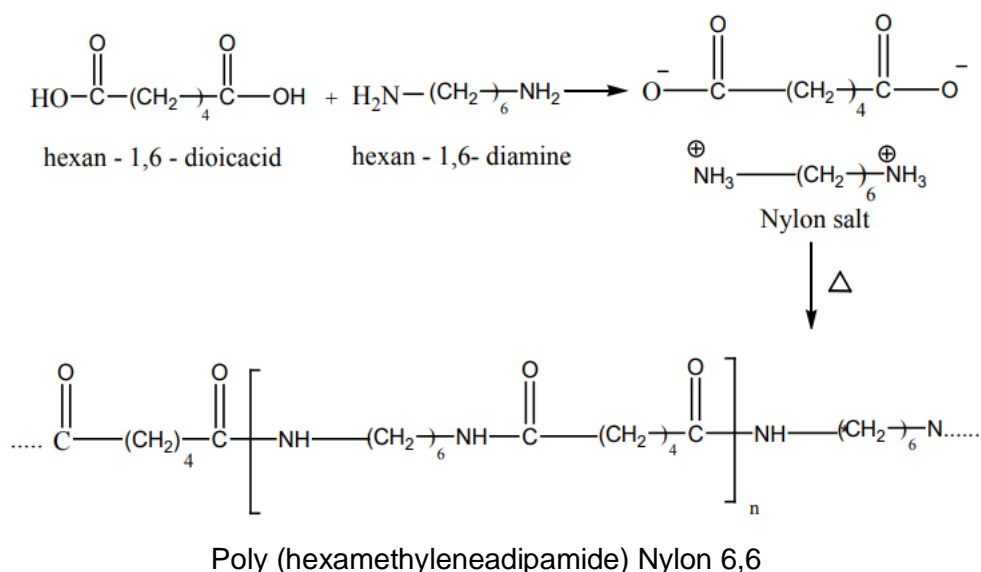


POLYMERS

Macromolecules, both natural and man-made, owe their great size to the fact that they are polymers (Greek: many parts); that is, each one is made up of a great many simpler units identical to each other or at least chemically similar joined together in a regular way. They are formed by a process we touched on earlier: polymerization, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

Preparation of nylon (6, 6):

Nylon – 6, 6 can be prepared by mixing equimolar adipic acid and hexamethylene – diamine to form nylon salts which on heating eliminate a water molecule to form amide bonds.

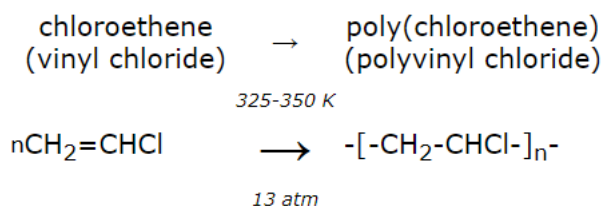


USES:

1. It is used in making the bristles of brushes.
2. It is also used to make Fabrics and carpets.

PREPARATION OF VINYL POLYMERIZATION:

For the preparation of polyvinylchloride, the monomer used is vinyl chloride (CH₂=CHCl). Polyvinyl chloride is prepared by addition polymerisation in which monomers are added in a chain. Vinyl chloride is treated with peracid under pressure and we get polyvinyl chloride (PVC).

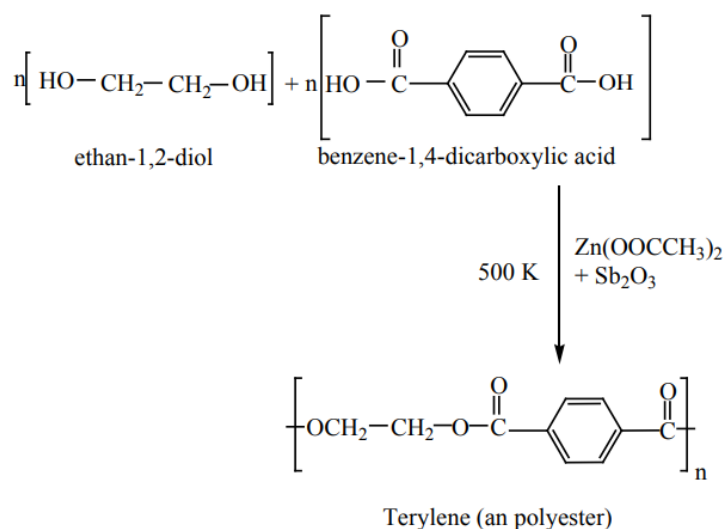


USES:

1. It is used for sewerage pipes and other pipe applications where cost or vulnerability to corrosion limit the use of metal.
2. With the addition of impact modifiers and stabilizers, it has become a popular material for window and door frames.
3. By adding plasticizers, it can become flexible enough to be used in cabling applications as a wire insulator.

PREPARATION OF TERYLENE (DACRON):

The monomers are ethylene glycol and terephthalic acid (or) dimethylterephthalate. When these monomers are mixed and heated at 500K in the presence of zinc acetate and antimony trioxide catalyst, terylene is formed.



USES:

1. Terylene is mainly used in making plastic bottles and clothing.
2. It is also used for making- Terylene fiber is used as polyester tericot knit as a fashion garments fabric.



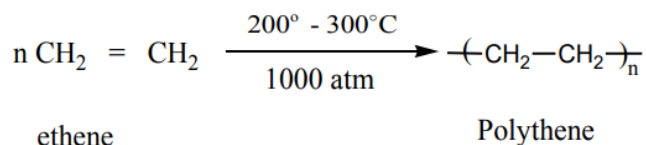
- Used for the laundry usage as a automatic clothing vacuum packaging machine.
- It is used to make non woven needle punched carpet particularly for the exhibition use.

PREPARATION OF POLYTHENE:

Polythene is an addition polymer of ethene. There are two types of polyethylene

- HDPE (High Density Polyethylene)
- LDPE (Low Density polyethylene).

LDPE :It is formed by heating ethene at 200 to 300 °C under oxygen as a catalyst. The reaction follows free radical mechanism. The peroxides formed from oxygen acts as a free radical initiator.



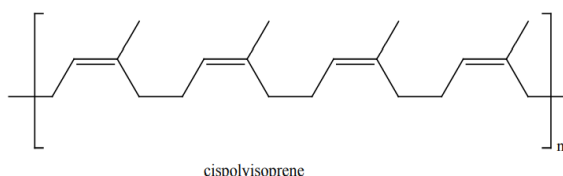
HDPE: The polymerization of ethylene is carried out at 373K and 6to7 atm pressure using Zeiglar – Natta catalyst [TiCl₄ + (C₂ H₅)₃Al] HDPE has high density and melting point .

USES:

- It is used to make bottles, pipe etc..,
- It is used as insulation for cables, making toys etc

NATURAL AND SYNTHETIC RUBBERS:

Rubber is a naturally occurring polymer. It is obtained from the latex that excludes from cuts in the bark of rubber tree (Ficus elastic). The monomer unit of natural rubber is cis- isoprene (2-methyl buta-1,3-diene). Thousands of isoprene units are linearly linked together in natural rubber. Natural rubber is not so strong or elastic. The properties of natural rubber can be modified by the process called vulcanization.



Vulcanization: Cross linking of Rubber

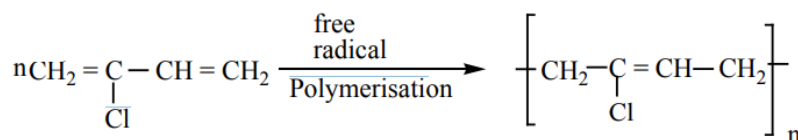


Natural rubber is mixed with 3-5% sulphur and heated at 100-150°C causes cross linking of the cis-1, 4-polyisoprene chains through disulphide (-S-S-) bonds. The physical properties of rubber can be altered by controlling the amount of sulphur that is used for vulcanization. In sulphur rubber, made with about 1 to 3% sulphur is soft and stretchy. When 3 to 10% sulphur is used the resultant rubber is somewhat harder but flexible.

SYNTHETIC RUBBER:

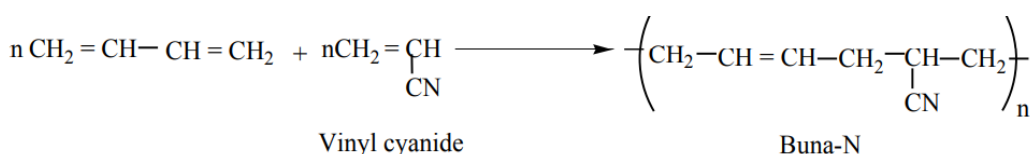
Polymerization of certain organic compounds such as buta-1, 3-diene or its derivatives gives rubber like polymer with desirable properties like stretching to a greater extent etc., such polymers are called synthetic rubbers.

Preparation of Neoprene: The free radical polymerization of the monomer, 2-chloro buta-1, 3-diene (chloroprene) gives neoprene. It is superior to rubber and resistant to chemical action.



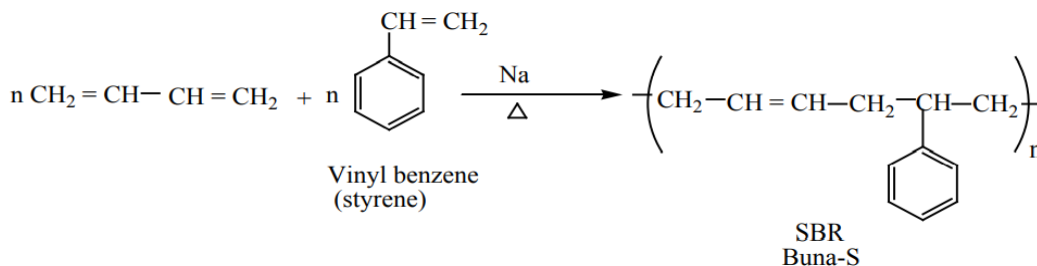
Uses: It is used in the manufacture of chemical containers, conveyer belts.

Preparation of Buna-N: It is a co-polymer of acrylonitrile and buta-1,3-diene



Uses: It is used in the manufacture of hoses and tank linings.

Preparation of Buna-S: It is a co-polymer. It is obtained by the polymerisation of buta-1, 3-diene and styrene in the ratio 3:1 in the presence of sodium.

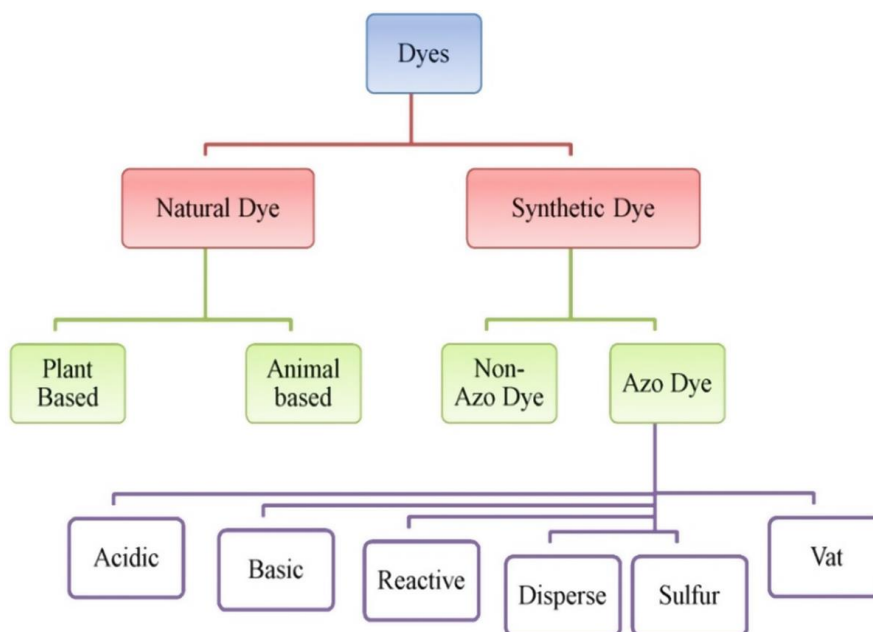


DYES

Dyes are organic compounds which are widely used for imparting colour to textiles. They are produced either chemically or from plants.

CLASSIFICATION OF DYES:

Dyes can be mainly classified into two different class that is Natural and synthetic dyes. Further it is classified based on the origin and the chemical reactions and their natures etc.



NATURAL DYE:



Dyes, as stated earlier, can be obtained from natural sources such as vegetable matter, mineral or insects or are manufactured in the factory from petrochemical feedstock. Amongst natural dyes, indigo is well known for its brilliant blue colour and was obtained by fermenting the leaves of a plant. The red coloured lac dye is extracted from lac, a resinous protective secretion of a tiny insect.

SYNTHETIC DYES:

I Direct Dyes:(Non- Azo dyes)

- Direct dyes are cheap and easy to apply, but of poor fastness quality.
- These dyes are also known as ‘salt dyes’ or cotton colours, which dye cotton, other vegetable fibres and viscose rayon.
- They are readily soluble in water. Colours of cotton fabrics dyed with direct dyes are not fast.
- They are applied to Cellulose fibres from aqueous liquor in which an electrolyte is added, which is usually Sodium Chloride as it accelerates the rate at which the dye is picked up by the fibre.
- They generally bleed. To make them fast on fabric add Sodium Bicarbonate for warm colours, and Copper Sulphate for cool colours.

II AZO DYES:

(i) Acid dyes:

- These are soluble in water and are applied under acidic conditions.
- The acid dyestuff is mostly used for wool and silk and to a less extent nylon and acrylic fibres.
- The maximum quantity of dye absorbed depends on the amount of H₂SO₄ present in the bath.
- Acid dyes are inexpensive dyes.
- They are fast to light, but they are not fast to washing.



Acid dyes

(ii)Vat dyes:

- They are insoluble in water, but they are made soluble by the use of a strong reducing agent, such as Sodium hydrosulphite dissolved in sodium hydroxide



Vat dyes



- These are the fastest dyes for cotton, linen and rayon.
- They also may be applied to wool, nylon, polyester etc.
- Vat dyes are hot water dyes. • Hot water dyes are available in both powder and liquid form.
- The first synthetic Vat dye was an Indigo created in 1879.
- Vat dyes are expensive because of the initial cost as well as the method of application.

(iii)Azoic dyes:

The Azoic colours are applied to cotton in two stages. The first consists of treatment with naphthol and the second by treatment of the naphtholated material with diazotized base or diazotized salt. The colour development takes place in-situ by the coupling reaction between naphthol and diazo component.

- They are quite fast to washing and have poor to excellent light fastness.
- Azoic colours are used mostly on cotton and for special purposes on nylon
- Azoic colours are sometimes referred to as ice dyes because ice is frequently used to bring the dyes to low temperatures.



Azoic colours

- Azoic colours give bright, high intensity colours, much more so than the common dye classes.
- These are cold water dyes and are most suitable for cold dyeing techniques such as Batik, Tie-Dye, etc.

(iv) Basic dyes:

- The first coal tar dye was a basic dye.
- It is applied to wool, silk, cotton, acrylic, and modacrylic fibres.
- When acrylic fibres were first marketed, they were very difficult to dye due to lack of specific dye sites in the fibres. Such groups were introduced into the fibre and brilliant colours can now be obtained with these dyes.
- They give good fastness and bright shades to acrylics.



Basic dyes

(v) Reactive dyes:



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PAGE 63 OF 77

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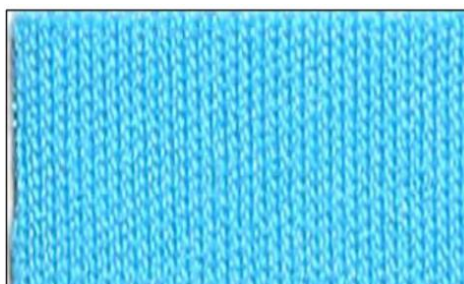
- The dye is retained by means of a chemical reaction between the dye and the fibre. As such their fastness properties are excellent.
- The fibres most readily coloured with reactive dyes are natural and manmade cellulosic fibres, natural protein fibres and polyamide fibres.
- With some reactive dyes, the dyeing can be carried out at room temperature. However with most reactive dyes, the dyeing is carried out at high temperatures (up to the boil).



Reactive dyes

(vi) Disperse dyes:

- The fibres that are most commonly dyed with disperse dyes are cellulose diacetate, cellulose triacetate and polyester fibres. To a lesser extent acrylic and nylon fibres are also dyed with disperse dyes.
- Polyester fibres being hydrophobic and with significant crystalline content, the assistance of high temperature, high pressure and carriers (which swell the fibre) is taken to achieve satisfactory dyeing.



Disperse dyed fabric

(vi) Sulphur dyes:

Natural and manmade cellulosic fibres are readily dyed with Sulphur dyes.

- Water soluble or leuco form of the dye is produced through reduction of the dye with Sodium Sulphide or Sodium Hydrosulphite.
- The dye liquor is heated to obtain satisfactory rate of dyeing
- Once the dye is within the fibre, the reduced Sulphur dye is converted to its original insoluble form by oxidation with an oxidizing agent like Sodium perborate.

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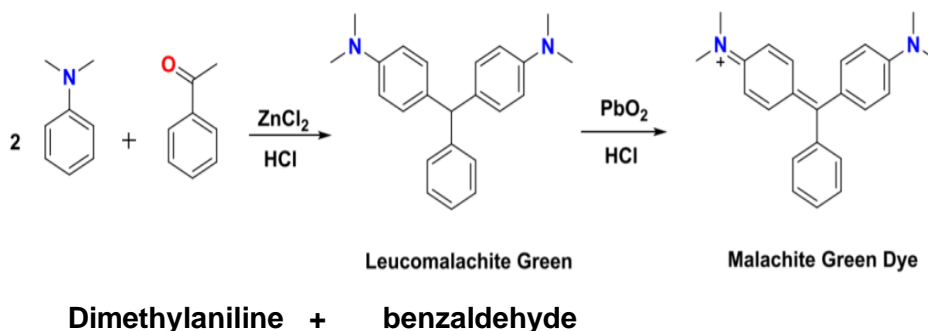
Sulphur dyes

Important dyes:

MALACHITE GREEN DYE:

- It is a type of triphenylmethane dyes bright green in color.
- Can be applied directly to wool & silk.
- By addition of mordant, can be applied to cotton.

Preparation of Malachite Green dye:



USES:

- (i) As spot test reagent for detection of sulphuric acid and cerium.
- (ii) As an antiseptic for bacterial infections.

Physical properties:

1. The crystals are bright green in colour, translucent, with a vitreous to adamantine lustre.
2. Malachite is one of a small number of green minerals that produces effervescence in contact with cold, dilute hydrochloric acid.
3. Malachite a high specific gravity that ranges from 3.6 to 4.0.

PHENOLPHTHALEIN DYE:

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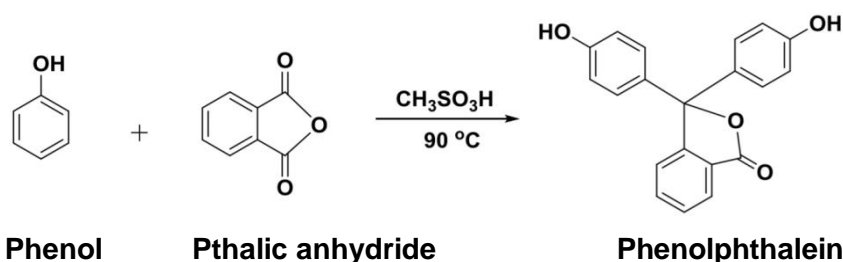
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Phenolphthalein is an organic compound used as a laboratory reagent and pH indicator. Phenolphthalein exerts laxative effects by stimulating the intestinal mucosa and constricting smooth muscles. However, phenolphthalein is no longer used as a laxative due to the suspected carcinogenicity of this compound. It belongs to class of dyes known as phthalein dyes.

Preparation :

Phenolphthalein can be prepared by reaction of phenol with phthalic anhydride.



Properties:

1. Phenolphthalein is slightly soluble in water and usually is dissolved in alcohols for use in experiments.
2. It is either yellowish-white to pale orange or white fine crystalline powder and in its liquid form it appears as a colourless till PH 8.5 and above that it appears as pink to deep red.
3. It does not have taste and smell.

Uses:

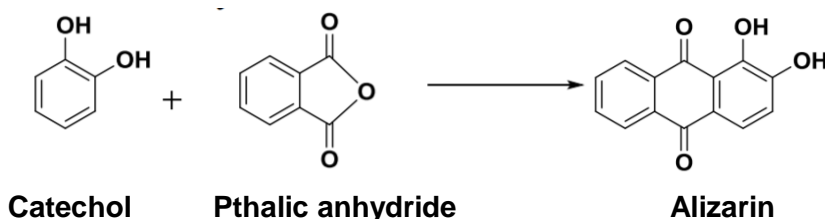
1. This chemical compound is widely used as PH indicator and laboratory agent.
2. Phenolphthalein is often used as an indicator in acid–base titrations. For this application, it turns colorless in acidic solutions and pink in basic solutions.

ALIZARIN DYE

The compound alizarin comes from the root of the madder plant. It is used as a dye to color fabrics. Alizarin can also be used as a pH indicator.

Preparation:

Alizarin is obtained when catechol is condensed with the phthalic anhydride in the presence of the anhydrous Aluminium chloride or conc. sulphuric acid at 140-150°C.



Properties:

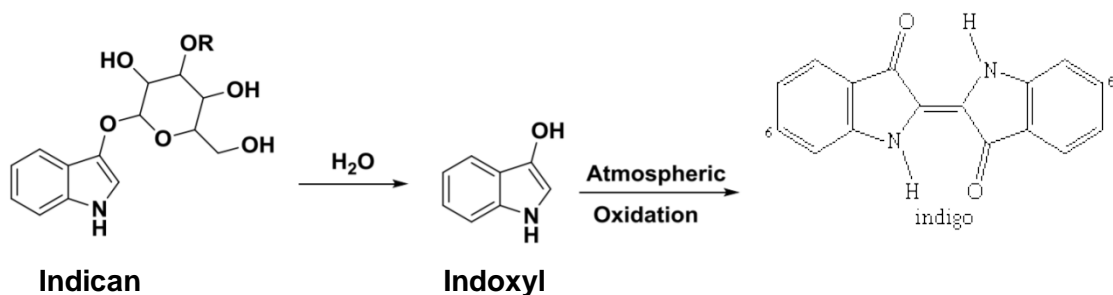
1. Alizarin is an orangish red powder.
2. It is partially dissolved in water.
3. It catches fire on contact with flames.
4. It get irritates with skin and eye if it is in contact.

Uses:

1. Alizarin continues to be used commercially as a red textile dye
2. Alizarin Red S is used to stain or locate calcium deposits in tissues.

INDIGO DYE:

Indigo has been known since ancient times and originally came from a plant extract. Plants of the Indigofera genus contain a glycoside called indican in their leaves and stems, which are extracted and acid hydrolyzed into indoxyl. Mild oxidation in atmospheric oxygen will then produce indigo.



Properties:

1. It is insoluble in water, alcohol or ether but soluble in DMSO, chloroform, nitrobenzene, and concentrated sulfuric acid.
2. Indigo is a dark blue crystalline powder that sublimates at 390–392 °C.



USES :

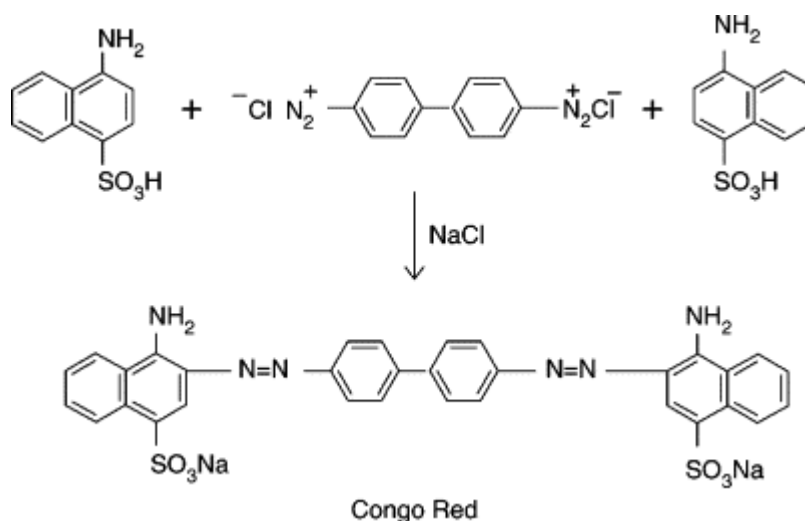
1. The primary use for indigo is as a dye for cotton yarn, mainly used in the **production** of denim cloth suitable for blue jeans.
2. Smaller quantities are used in the dyeing of wool and silk.
3. The Indigo Leaves are used to make hair dye as well as prepare medicated hair oil.
4. Leaf powder is used as natural black colour dye for hair.
5. Indigofera make your hair more manageable, moisturized, and protected with radiant shine.

CONGO RED DYE:

Congo red is an organic compound, the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid).

Preparation:

It is prepared by azo coupling of the bis(diazonium) derivative of benzidine with naphthionic acid.



Properties:

1. It is an azo dye.
2. Congo red is water-soluble, yielding a red colloidal solution; its solubility is greater in organic solvents. However, the use of Congo red has long been abandoned, primarily because of its carcinogenic properties.



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REV. NO. : **R0**
DATE : **18/08/2020**
COPY :
PAGE 63 OF 77

Edition : 1

Uses:

1. Congo red can be used as a pH indicator. Since this colour change is an approximate inverse of that of litmus, it can be used with litmus paper in a simple parlour trick

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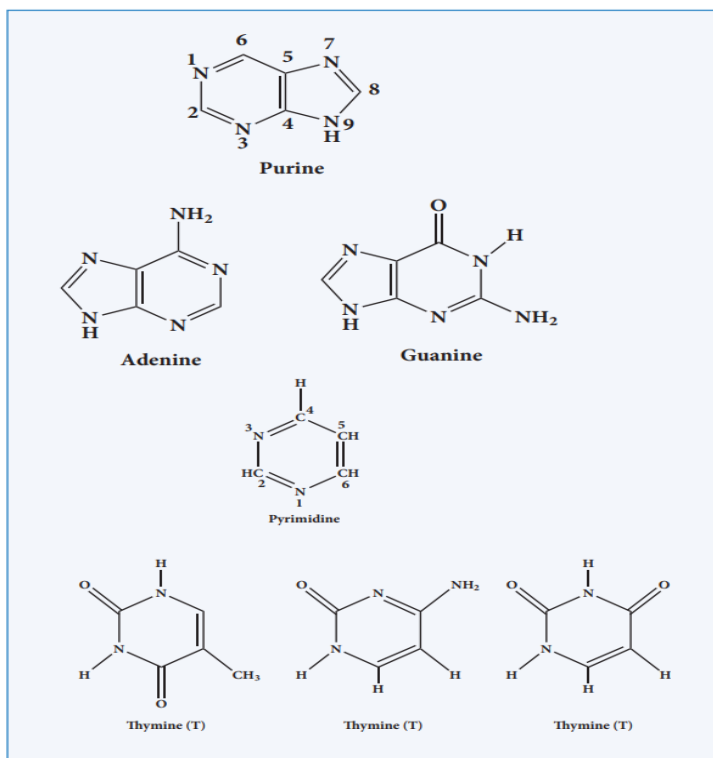
NUCLEIC ACID:

The inherent characteristics of each and every species are transmitted from one generation to the next. It has been observed that the particles in nucleus of the cell are responsible for the transmission of these characteristics. They are called chromosomes and are made up of proteins and another type of biomolecules called nucleic acids.

There are mainly two types nucleic acids, the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). They are the molecular repositories that carry genetic information in every organism. Composition and structure of nucleic acids Nucleic acids are biopolymers of nucleotides. Controlled hydrolysis of DNA and RNA yields three components namely a nitrogenous base, a pentose sugar and phosphate group.

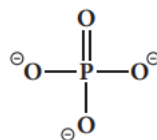
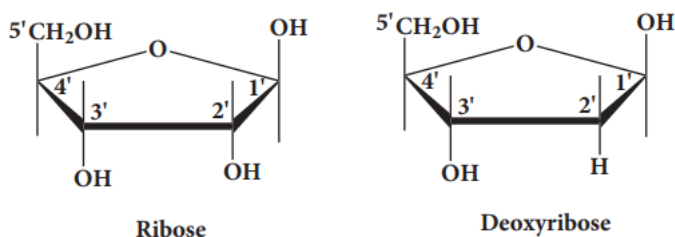
Nitrogen base:

These are nitrogen containing organic compounds which are derivatives of two parent compounds, pyrimidine and purine. Both DNA and RNA have two major purine bases, adenine (A) and guanine (G). In both DNA and RNA, one of the pyrimidines is cytosine (C), but the second pyrimidine is thymine (T) in DNA and uracil (U) in RNA.





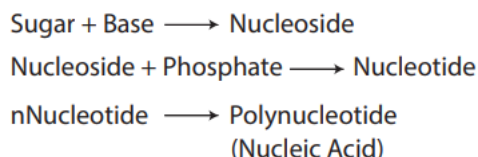
Pentose sugar: Nucleic acids have two types of pentose. The recurring deoxyribonucleotide units of DNA contain 2'-deoxy-D-ribose and the ribonucleotide units of RNA contain D-ribose. In nucleotides, both types of pentose are in their β -furanose (closed five membered rings) form.



Phosphate group: Phosphoric acid forms phosphor diester bond between nucleotides. Based on the number of phosphate group present in the nucleotides, they are classified into mono nucleotide, dinucleotide and trinucleotide.

NUCLEOSIDES AND NUCLEOTIDES:

The molecule without the phosphate group is called a nucleoside. A nucleotide is derived from a nucleoside by the addition of a molecule of phosphoric acid. Phosphorylation occurs generally in the 5' OH group of the sugar. Nucleotides are linked in DNA and RNA by phospho diester bond between 5' OH group of one nucleotide and 3' OH group on another nucleotide.



Ribose Nucleic Acids:

Most cellular RNA is single stranded, although some viruses have double stranded RNA. The single RNA strand is folded upon itself, either entirely or in certain regions. In the folded region a majority of the bases are complementary and are joined by hydrogen bonds. This helps in the stability of the molecule. In the unfolded region the bases have no complements. Because of this RNA does not have the purine, pyrimidine equality that is found in DNA.



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REV. NO. : **R0**
DATE : **05/04/2020**
COPY :
PAGE 78 OF 90

Edition : 1

RNA also differs from DNA in having ribose as the sugar instead of deoxyribose. The common nitrogenous bases of RNA are adenine, guanine, cytosine and uracil. Thus the pyrimidine uracil substitutes thymine of DNA. In regions where purine pyrimidine pairing takes place, adenine pairs with uracil and guanine with cytosine. In addition to the four bases mentioned above, RNA also has some unusual bases.

RNA molecules are classified according to their structure and function into three major types i. Ribosomal RNA (rRNA) ii. Messenger RNA (mRNA) iii. Transfer RNA (tRNA).

Ribosomal rRNA:

rRNA Ribosomal RNA, as the name suggests, is found in the ribosomes. It comprises about 80% of the total RNA of the cell. The base sequence of rRNA is complementary to that of the region of DNA where it is synthesized. In eukaryotes ribosomes are formed on the nucleolus. Ribosomal RNA is formed from only a small section of the DNA molecule, and hence there is no definite base relationship between rRNA and DNA as a whole. Ribosomal RNA consists of a single strand twisted upon itself in some regions. It has helical regions connected by intervening single strand regions.

The helical regions may show presence or absence of positive interaction. In the helical region most of the base pairs are complementary, and are joined by hydrogen bonds. In the unfolded single strand regions the bases have no complements. Ribosomal RNA contains the four major RNA bases with a slight degree of methylation, and shows differences in the relative proportions of the bases between species. Its molecules appear to be single polynucleotide strands which are unbranched and flexible. At low ionic strength rRNA behaves as a random coil, but with increasing ionic strength the molecule shows helical regions produced by base pairing between adenine and uracil and guanine and cytosine.

Transfer tRNA:

tRNA molecules have lowest molecular weight of all nucleic acids. They consist of 73 – 94 nucleotides in a single chain. The function of tRNA is to carry amino acids to the sites of protein synthesis on ribosomes.

Structure of Transfer RNA :

tRNA's are L-shaped molecules. The amino acid is attached to one end and the other end consists of three anticodon nucleotides. The anticodon pairs with a codon in messenger RNA (mRNA) ensuring that the correct amino acid is incorporated into the growing polypeptide chain. The L-shaped

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tRNA is formed from a small single-stranded RNA molecule that folds into the proper conformation. Four different regions of double-stranded RNA are formed during the folding process.

Messenger mRNA:

mRNA is present in small quantity and very short lived. They are single stranded, and their synthesis takes place on DNA. The synthesis of mRNA from DNA strand is called transcription. mRNA carries genetic information from DNA to the ribosomes for protein synthesis. This process is known as translation.

Stability of Messenger RNA:

mRNA - The cell does not contain large quantities of mRNA. This is because mRNA, unlike other RNAs is constantly undergoing breakdown. It is broken down to its constituent ribonucleotides by ribonucleases. Structure of Messenger RNA - mRNA Messenger RNA is always single stranded. It contains mostly the bases adenine, guanine, cytosine and uracil. There are few unusual substituted bases. Although there is a certain amount of random coiling in extracted mRNA, there is no base pairing. In fact base pairing in the mRNA strand destroys its biological activity Since mRNA is transcribed on DNA (genes), its base sequence is complementary to that of the segment of DNA on which it is transcribed. This has been demonstrated by hybridization experiments in which artificial RNA, DNA double strands are produced. Hybridization takes place only if the DNA and RNA strands are complementary.

COMPARISON OF RNA AND DNA:

	DNA	RNA
1.	DNA is the usual genetic material	RNA is the genetic material of some viruses.
2.	DNA is usually double-stranded, (In certain viruses DNA is single stranded, e.g. ϕ X 174).	Most cellular RNA is single stranded. (Some viruses e.g. retrovirus, have double stranded RNA).
3.	The pentose sugar is deoxyribose.	The pentose sugar is ribose.
4.	The common organic bases are adenine, guanine, cytosine and thymine.	The common organic bases are adenine, guanine, cytosine and uracil.
5.	Base pairing: adenine pairs with thymine and guanine with cytosine.	Adenine pairs with uracil and guanine with cytosine.

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DRUGS

A very broad definition of a drug would include “all chemicals other than food that affect living processes.” If the affect helps the body, the drug is a medicine. However, if a drug causes a harmful effect on the body, the drug is a poison.

Another definition would be “medicinal agents used for diagnosis, prevention, treatment of symptoms, and cure of diseases.”

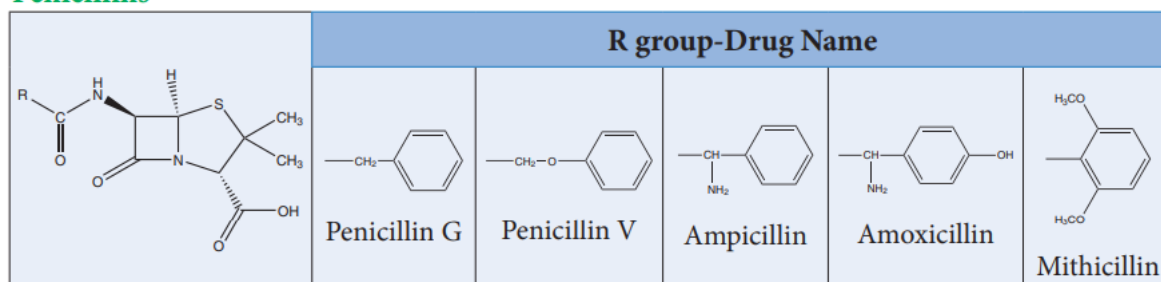
Classification of drugs:

Drugs are classified based on their properties such as chemical structure, pharmacological effect, target system, site of action etc.

Classification based on the chemical structure:

In this classification, drugs with a common chemical skeleton are classified into a single group. For example, ampicillin, amoxicillin, methicillin etc. All have similar structure and are classified into a single group called penicillin. Similarly, we have other group of drugs such as opiates, steroids, catechol amines etc. Compounds having similar chemical structure are expected to have similar chemical properties. However, their biological actions are not always similar. For example, all drugs belonging to penicillin group have same biological action, while groups such as barbiturates, steroids etc... have different biological action.

Penicillins



Classification based on Pharmacological effect:

In this classification, the drugs are grouped based on their biological effect that they produce on the recipient. For example, the medicines that have the ability to kill the pathogenic bacteria are grouped as antibiotics. Examples: Antibiotic drugs: amoxicillin, ampicillin, cefixime, cefpodoxime, erythromycin, tetracycline etc.. Antihypertensive drugs: propranolol, atenolol, metoprolol succinate, amlodipine etc...



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DOCUMENT NO. : **DCG 016**
REV. NO. : **R0**
DATE : **05/04/2020**
COPY :
PAGE 78 OF 90

Edition : 1

Classification based on the target system (drug action):

In this classification, the drugs are grouped based on the biological system/process that they target in the recipient. For example; the antibiotics streptomycin and erythromycin inhibit the protein synthesis (target process) in bacteria and are classified in a same group. However, their mode of action is different. Streptomycin inhibits the initiation of protein synthesis, while erythromycin prevents the incorporation of new amino acids to the protein.

Classification based on the site of action (molecular target):

The drug molecule interacts with biomolecules such as enzymes, receptors etc., which are referred as drug targets. We can classify the drug based on the drug target with which it binds. This classification is highly specific compared to the others. These compounds often have a common mechanism of action, as the target is the same.

Drug–target Interaction:

The biochemical processes such as metabolism (which is responsible for breaking down the food molecules and harvest energy in the form of ATP and biosynthesis of necessary bio molecules from the available precursor molecules using many enzymes), cell-signalling (senses any change in the environment using the receptor molecules and send signals to various processes to elicit an appropriate response) etc... are essential for the normal functioning of our body.

These routine processes may be disturbed by any external factors such as microorganism, chemicals etc., or by a disorder in the system itself. Under such conditions we may have to take medicines to restore the normal functioning of the body. These drug molecules interact with bio molecules such as proteins, lipids, etc., that are responsible for different functions of the body. For example, proteins which act as biological catalysts are called enzymes and those which are important for communication systems are called receptors. The drug interacts with these molecules and modifies the normal biochemical reactions either by modifying the enzyme activity or by stimulating/suppressing certain receptors.

SITES OF DRUG ACTION:

I. Enzyme inhibition: Drugs act within the cell by modifying normal biochemical reactions. Enzyme inhibition may be reversible or non-reversible; competitive or non-competitive. Anti-metabolites may be used which mimic natural metabolites.

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DOCUMENT NO. : **DCG 016**
REV. NO. : **R0**
DATE : **05/04/2020**
COPY :
PAGE 78 OF 90

Edition : 1

2. Drug-Receptor interaction: Drugs act on the cell membrane by physical and/or chemical interactions. This is usually through specific drug receptor sites known to be located on the membrane. A receptor is the specific chemical constituents of the cell with which a drug interacts to produce its pharmacological effects. Some receptor sites have been identified with specific parts of proteins and nucleic acids. In most cases, the chemical nature of the receptor site remains obscure.

3. Non-specific interactions: Drugs act exclusively by physical means outside of cells. These sites include external surfaces of skin and gastrointestinal tract. Drugs also act outside of cell membranes by chemical interactions. Neutralization of stomach acid by antacids is a good example

MODE OF DRUG ACTION:

It is important to distinguish between actions of drugs and their effects. Actions of drugs are the biochemical's, physiological mechanisms by which the chemical produces a response in living organisms. The effect is the observable consequence of a drug action. For example, the action of penicillin is to interfere with cell wall synthesis in bacteria and the effect is the death of bacteria.

MECHANISM OF DRUG ACTION:

A drug act by virtue of its various properties like physical, chemical, physiological etc. The fundamental mechanisms of drug action can be distinguished into following categories.

1. Physical Properties:

A physical property of the drug is responsible for its action. (i) Taste. Bitter taste drugs increase the flow the hydrochloric acid reflexly in the stomach. Ex: Quassia, Chirata (ii) Mass. By increasing the bulk of drug in intestine produce laxative effect. Ex: Isapgol (iii) Adsorption. Certain drugs like kaolin adsorb water on to its surface and there by reduce gastric motility (iv) Radioactivity. The radioactive substances are commonly used to treat cancer.

2. Chemical Properties:

The drugs react extracellularly according to simple chemical reactions like neutralization, chelation, oxidation etc. Ex: (i) Aluminium hydroxide neutralizes acid in stomach (ii) Toxic heavy metals can be eliminated by chelating agents like EDTA, BAL, penicillamine etc. (iii) Oxidising agents are germicidal.

3. Through Enzymes:

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DATE : **28/08/2020**



Enzymes are very important targets of drug action because almost all biological reactions are carried out under the influence of enzymes. Drugs may either increase or decrease enzymatic reactions. Ex: (i) Adrenaline stimulates adenyl cyclase (ii) Pyridoxine acts as a cofactor and increases decarboxylase activity (iii) Allopurinol competes with hypoxanthine for xanthine oxidase (iv) Physostigmine and neostigmine compete with acetylcholine for cholinesterase.

4. Through Receptors:

A large number of drugs act through specific macromolecular components of the cell, which regulate critical functions like enzymatic activity, permeability, structural features, template function etc. These macromolecules, which bind and interact with the drugs, are called receptors.

THERAPEUTIC ACTION OF DIFFERENT CLASSES OF DRUGS:

I ANTISEPTIC (DETTOL):

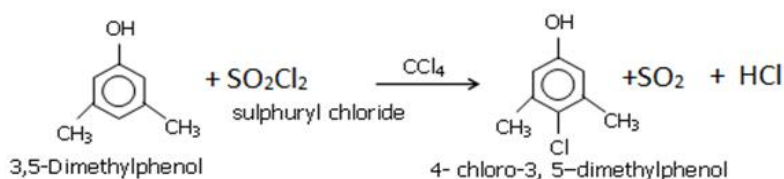
Class of Drugs: Antiseptic Example: Dettol

Mode of action: Stop or slow down the growth of microorganisms – Applied to living tissue

Chemical name: 4-chloro-3,5-dimethylphenol (Chloroxylenol)

Preparation of Dettol:

Dettol can be prepared by treating 3,5-dimethyl phenol with thionyl chloride in the presence of carbon tetrachloride gives 4-chloro-3,5-dimethylphenol (Chloroxylenol)



(Chloroxylenol)

Uses: (i) Chloroxylenol is used in hospitals and households for disinfection and sanitation.

(ii) It is also commonly used in antibacterial soaps, wound-cleansing applications and household antiseptics such as

Dettol liquid

II ANTIPYRETIC (PARACETAMOL):

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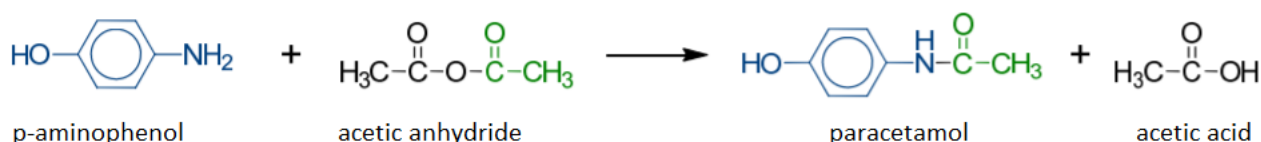
Class of Drugs: Antipyretic Example: paracetamol

Mode of action: Paracetamol has a central analgesic effect that is mediated through activation of descending serotonergic pathways. These drugs have many other effects such as reducing fever (antipyretic)

Chemical name: acetaminophen

Preparation of Paracetamol:

Paracetamol is made by reacting 4-aminophenol with ethanoic anhydride.



Uses:

(i) Paracetamol is a common painkiller used to treat **aches** and **pain**. It can also be used to reduce a high temperature.

(ii) Used for short-term pain relief and for modest pain like headache, muscle strain, bruising, or arthritis.

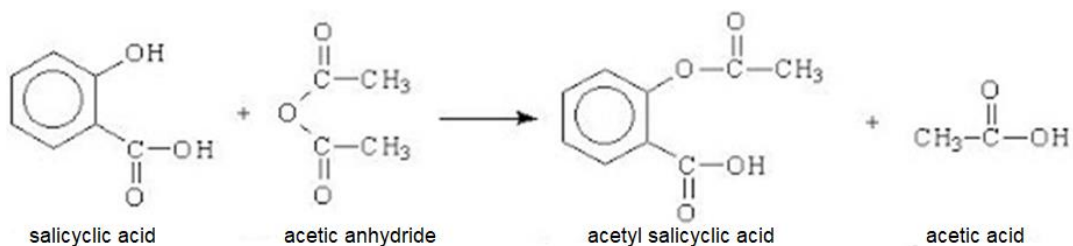
III ANALGESIC (ASPIRIN):

Class of Drugs: Analgesic Example: Aspirin

Mode of action: Aspirin and other non-steroid anti-inflammatory drugs (NSAIDs) inhibit the activity of the enzyme now called cyclooxygenase (COX) which leads to the formation of prostaglandins (PGs) that cause inflammation, swelling, pain and fever.

Chemical name: Acetylsalicylic acid

Preparation of Aspirin: To prepare aspirin, salicylic acid is reacted with an excess of acetic anhydride. A small amount of a strong acid is used as a catalyst which speeds up the reaction.





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DOCUMENT TITLE
**UNIT -V
NUCLEIC ACID AND DRUGS**

DOCUMENT NO. : **DCG 016**
REV. NO. : **R0**
DATE : **05/04/2020**
COPY :
PAGE 78 OF 90

Edition : 1

Uses: (i) These drugs have many other effects such as reducing fever (antipyretic) and preventing platelet coagulation. Due to this property, aspirin finds useful in the prevention of heart attacks.

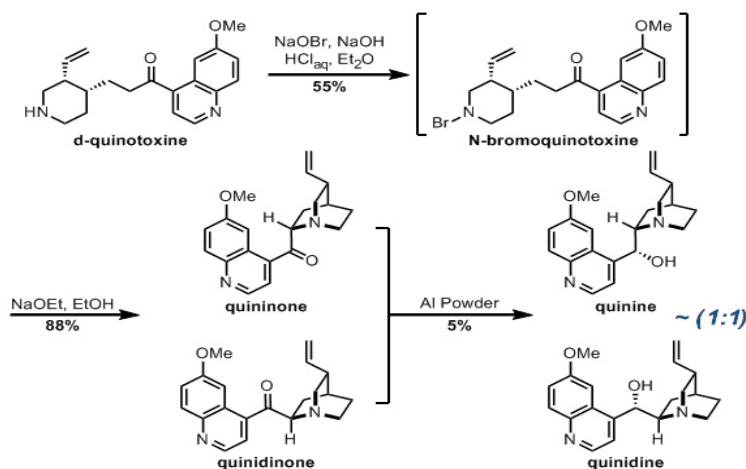
(ii) Reduces fever by causing the hypothalamus to override a prostaglandin-induced increase in temperature.

IV ANTIMALARIAL (QUININE):

Class of Drugs: Antimalarial Example: Quinine

Mode of action: Quinine inhibits nucleic acid synthesis, protein synthesis, and glycolysis in Plasmodium falciparum and can bind with hemazoin in parasitized erythrocytes.

Preparation of Quinine:



Uses:

Quinine is a medication used to treat malaria and babesiosis. This includes the treatment of malaria due to Plasmodium falciparum that is resistant to chloroquine.

V ANTIBIOTIC (PENICILLIN)

Class of Drugs: Antibiotic Example: Penicillin

Mode of action: Penicillin kills bacteria through binding of the beta-lactam ring to DD-transpeptidase, inhibiting its cross-linking activity and preventing new cell wall formation. Without a cell wall, a bacterial cell is vulnerable to outside water and molecular pressures, which causes the cell to quickly die.

Structure of Penicillin:

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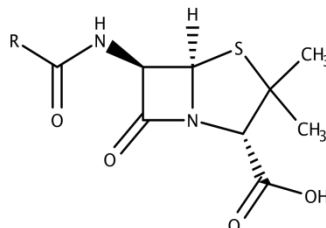
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DOCUMENT NO. : **DCG 016**
REV. NO. : **R0**
DATE : **05/04/2020**
COPY :
PAGE 78 OF 90

Edition : 1



Uses:

- (i) Penicillin V potassium is used to treat certain **infections** caused by bacteria such as pneumonia.
- (ii) Other respiratory tract infections, scarlet fever, and ear, skin, gum, mouth, and throat infections.

VI SULFA DRUG (SULFADIAZINE)

Class of Drugs: Sulfa Drug Example: Sulfadiazine

Mode of action: Sulfadiazine is a competitive inhibitor of the bacterial enzyme dihydropteroate synthetase. This enzyme is needed for the proper processing of para-aminobenzoic acid (PABA) which is essential for folic acid synthesis. The inhibited reaction is necessary in these organisms for the synthesis of folic acid.

Uses:

- (i) Sulfadiazine is an antibacterial prescription medicine
- (ii) Drug Administration (FDA) for the prevention and treatment of certain types of bacterial infections, including the treatment of chancroid, Toxoplasma gondii encephalitis, urinary tract infections, and other infections.

Structure of Sulfadiazine:

Sulfadiazine's is prepared as follows:

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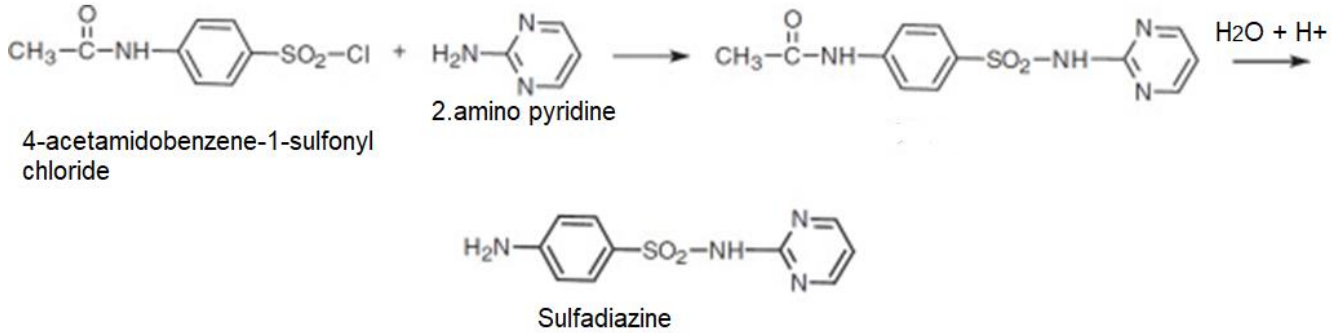
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DOCUMENT NO. : DCG 016
REV. NO. : R0
DATE : 05/04/2020
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PAGE 78 OF 90

Edition : 1



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PAGE 100 OF 115

Edition : 1

B.Sc. DEGREE EXAMINATION,
NOVEMBER / DECEMBER 2019.
Third semester
Physics
Allied: CHEMISTRY –I
(COMMON FOR ALL BRANCHES)
(From 2017 -18 onwards)

Time: 3 hrs

Maximum: 60 marks

PART A – (10 x 2 = 20)
Answer ALL the questions.

- Classify the following as electrophiles and nucleophiles.
(a) BF_3 -Electrophile (b) NH_3 - Nucleophile (c) Ag^+ - Electrophile (d) CN^- Nucleophile
- Write the structural formulae of the following compounds.
(a) 3-chloro propene - $\text{Cl}-\text{CH}_2-\text{CH}=\text{CH}_2$
(b) 2-methyl butane - $\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3$

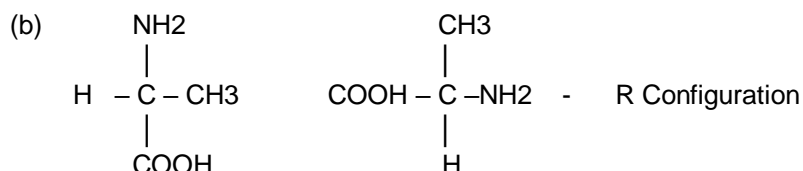
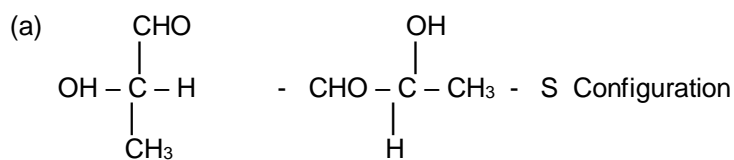


- What are the essential conditions for a molecule to be optically active?

The necessary and sufficient condition for a compound to be optically active is that

- It must contain asymmetric carbon atoms.
- Its molecule must be non-identical with its mirror image.
- It must be symmetric.
- Its molecule must be identical with its mirror image.

- Assign R and S configuration to the following molecules.



- Write the Henderson- Hasselbalch equation.

The Henderson–Hasselbalch equation can be used to estimate the pH of a buffer solution.

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$$\text{pH} = \text{p}K_a + \log_{10} \left(\frac{[\text{Base}]}{[\text{Acid}]} \right)$$

The numerical value of the acid dissociation constant, K_a , of the acid is known or assumed. The pH is calculated for given values of the concentrations of the acid, HA and of a salt, MA, of its conjugate base, A^- .

6. Define molarity and molality.

Molarity:

It is defined as the number of moles of the solute in 1 litre of the solution.

Thus, Molarity (M) = No. of moles of solute / Volume of solution in litres

Molality:

It is defined as the number of moles of solute present in 1 kg of solvent.

It is denoted by m. Thus, Molality (m) = No. of moles of solute / Mass of solvent in kg

7. Differentiate fertile and fissile nuclei with examples

S.NO	FISSILE ISOTOPES	FERTILE ISOTOPES
1	Fissile isotopes are atoms that can undergo fission reactions	Fertile isotopes are atoms that can convert into fissile isotopes
2	Converts into non-fissionable isotopes upon fission	Converts into fissionable isotopes upon the combination of neutrons
3	Can undergo fission reactions directly	Cannot undergo fission reactions directly
4	Uranium – 235, Plutonium -239 and Uranium -233	Thorium – 232 and Uranium -238

8. Write nuclear fusion and fission reactions.

When lighter nuclei moving at a high speed are fused together to form a heavy nucleus, the process is called **nuclear fusion**.

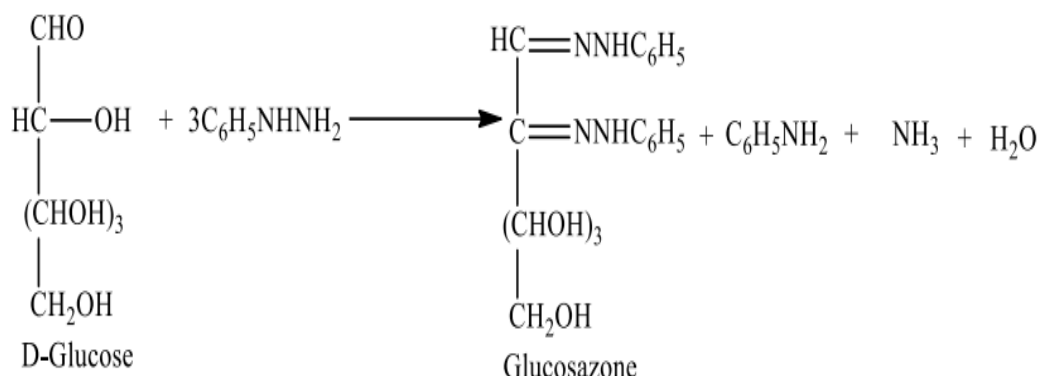
Nuclear fission is the process in which a heavy nucleus breaks up into two lighter nuclei of almost equal size with the release of an enormous amount of energy.

9. Which among the following is/are reducing carbohydrates?

(a) Sucrose - Non-reducing (b) glucose – Reducing (c) ribose - Reducing (d) fructose – Reducing

10. How is glucosazone obtained from glucose? Give the reaction.

When α -hydroxy carbonyl compounds react with three equivalents of phenylhydrazine to form bis-phenylhydrazones, commonly called osazones.



PART B – (4 X 5 = 20 MARKS)

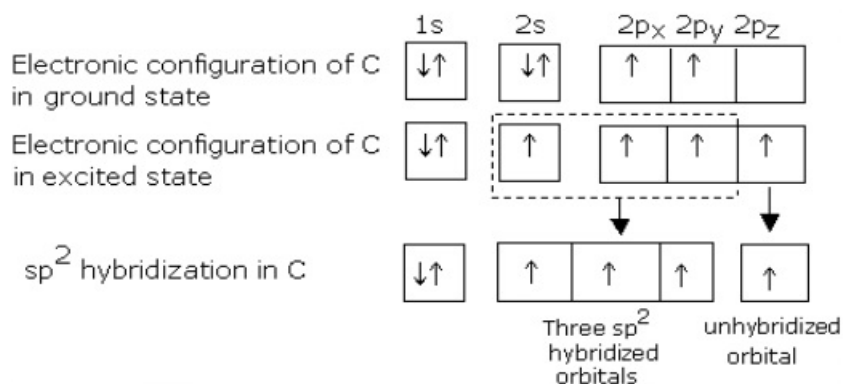
Answer ALL the questions, choosing either (a) or (b)

11. (a) Discuss the type of hybridisation found in ethylene.

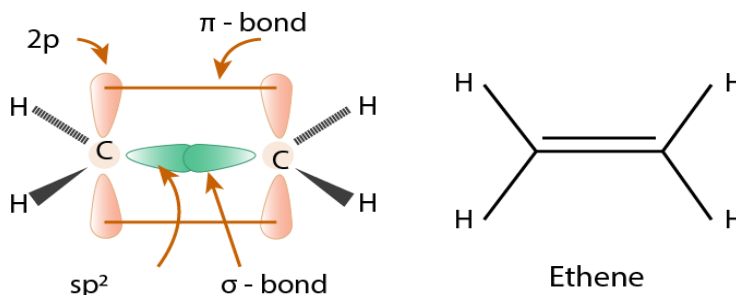
sp² Hybridization of carbon:

- In the formation of ethene two carbon atoms form one sigma bond by 'head-on' overlap of two sp² orbitals contributed one each by the two atoms.
- The remaining two sp² orbitals of each carbon form σ bonds with H atoms.
- The unhybridized 2p_z orbitals of the two carbon atoms undergo a side-wise overlap forming a π bond.
- Thus the carbon to carbon double bond in ethene is made of one σ bond and one π bond.

• **Formation of Ethene molecule(C₂H₄):**



Hybridisation in Ethene or ethylene:



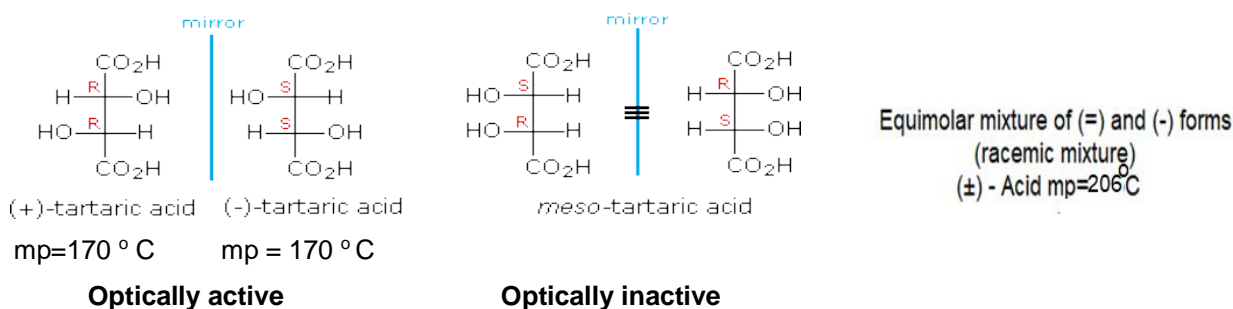
(OR)

(b) Differentiate between homolytic and heterolytic fission with suitable examples.

S.NO	HOMOLYTIC FISSION	HETEROLYTIC FISSION
1.	When the cleavage of covalent bond between two atoms takes place in a manner, which enables each atom to retain one electron of the shared pair, it is called homolytic fission.	When the cleavage of covalent bond between two atoms takes place in a manner, which enables each atom to retain both the electron of the shared pair, it is called heterolytic fission.
2.	 :Br-Br: → ·Br + ·Br	 :Br-Br: → :Br: + :Br:
3.	It is denoted by half arrow i.e fish hook arrow denotes sharing of one electron each.	It is denoted by full arrow denotes sharing of both electron by one atom.
4.	Rate of the reaction is fast.	It takes place in moderate rate.
5.	Formation of Free radicals takes place which are highly reactive	Ions are formed in this reaction with most electronegative and electropositive atom

12. (a) Discuss Optical Isomerism with special reference to tartaric acid:

Tartaric acid contains two asymmetric carbon atoms. The four different forms of Tartaric acid are shown below: Two of them are optically active and two are optically inactive. The optically active forms are related to each other as an object to its mirror image i.e., they are enantiomers.



1. (+)- Tartaric acid. It rotates the plane polarised light to the right (clockwise) and is called dextrorotatory.
2. (-)-Tartaric acid. It rotates the plane polarised light to the left (anticlockwise) and is called laevorotatory. Both are mirror image of each other.
3. Meso- Tartaric acid : It possesses a plane of symmetry and is consequently optically inactive.(internally compensated- Optical rotation of asymmetric carbon is cancelled by the other)
4. (±)-Tartaric acid. It does not rotate the plane of polarised light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

(OR)

(b) Explain the following terms:

(i) Enantiomers:

The non-super imposable mirror image forms a chiral molecules are called enantiomers.(optical isomers that are mirror images)

Characteristic features of Enantiomers:

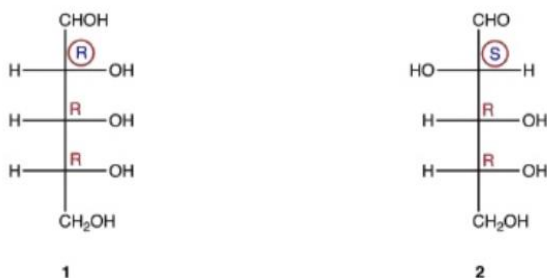
- Enantiomers have the same physical properties(bp ,mp, Density,solubility, etc..)
- Enantiomers will rotate plane polarized light the same magnitude (α) but opposite directions (+ or -).
- A mixture of equal amounts of two enantiomers is called a racemic mixture (optically inactive).A racemic mixture is a 50:50 mixture of two enantiomers.
- It cannot be interconverted under ordinary conditions.
- They have different biological properties .E.g. (+) - dextrose plays an important role in animal metabolism, whereas (-)-dextrose is not metabolized.
- A well know example is two isomers of Lactic acid (+ & -).

(ii)Diastereomers:

Stereoisomers of a substance that are not mirror images of each other are termed as Diastereomers.

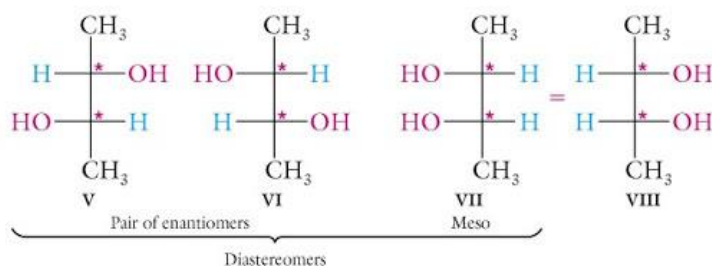
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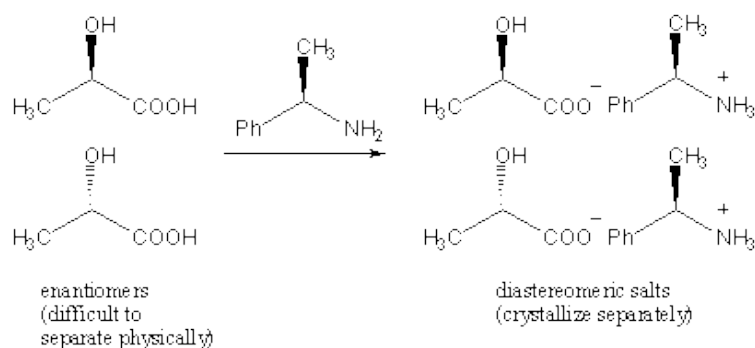
Characteristic features of Diastereomers:

- They have different physical properties like m.p, b.p, solubility, density, etc.
- They have different specific rotation but they may have same or opposite sign of rotation.



(ii) Resolution:

Separation of racemates into their component enantiomers is a process called resolution. Since enantiomers have identical physical properties, such as solubility and melting point, resolution is extremely difficult.

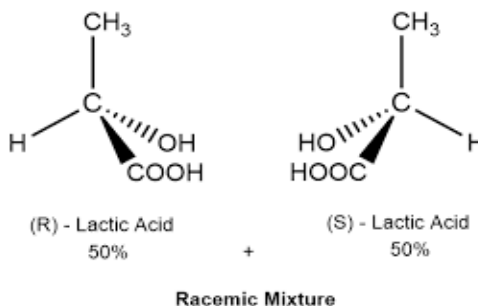


(iv) Racemisation:

Racemization is a conversion, by heat or by chemical reaction, of an optically active compound into a racemic (optically inactive) form. Half of the optically active substance becomes its mirror image (enantiomer) referred as racemic mixtures (i.e. contain equal amount of (+) and (-) forms). If the racemization results in a



mixture where the D and L enantiomers are present in equal quantities, the resulting sample is described as a racemic mixture or a racemate.



13. (a) Define the following terms.

- (i) Mole: Mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the ^{12}C isotope.
- (ii) ppm: Parts per million can be defined as the ratio of number of parts of the component to the total number of parts of all components of the solution multiplied by 10^6 . It is denoted by ppm.
- (iii) ppb: Parts per billion (ppb) is a term that expresses the number of units (parts) of a given substance that exist as a portion of a greater substance comprised of one billion parts.
- This measurement can be expressed as 1ppb, which is equal to 1×10^{-9}
- (iv) pH: It is defined as the negative of the base -10 logarithm (log) of the H^+ concentration. Mathematically it may be expressed as
- $$\text{pH} = -\log_{10} [\text{H}^+],$$
- where $[\text{H}^+]$ is the concentration of hydrogen ions in moles per litre.
- (v) Physiological buffer: Physiological buffers are chemicals used by the body to prevent large changes in the pH of a bodily fluid.

(OR)

(b) Derive the Henderson-Hasselbalch equation of buffer solution.

HENDERSON EQUATION:

The pH of an acid buffer can be calculated from the dissociation constant, K_a , of the weak acid and the concentrations of the acid and the salt used.

The dissociation expression of the weak acid, HA, may be represented as





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

$$\text{Or } [H^+] = \frac{[HA] K_a}{[A^-]} \quad \dots (1)$$

The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt ($Na^+ A^-$) which provides A^- ions (Common ion effect). As a result the equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration $[A^-]$ is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus we can write the equation (1) as

$$[H^+] = K_a \times [\text{acid}] / [\text{salt}] \quad \dots (2)$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used. Taking negative logs of both sides of the equation (2), we have

$$-\log [H^+] = -\log K_a - \log [\text{acid}] / [\text{salt}] \quad \dots (3)$$

But $-\log [H^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$

Thus from (3) we have

$$\text{pH} = \text{p}K_a - \log [\text{acid}] / [\text{salt}]$$

$$= \text{p}K_a + \log [\text{salt}] / [\text{acid}]$$

$$\text{Hence, } \text{pH} = \text{p}K_a + \log [\text{salt}] / [\text{acid}]$$

This relationship is called the Henderson-Hasselbalch equation or simply Henderson equation.

In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as :

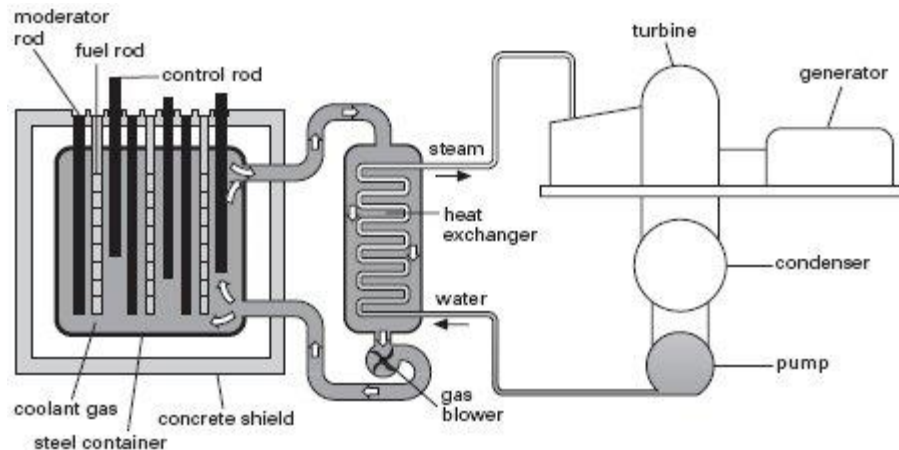
$$\text{pOH} = \text{p}K_b + \log [\text{salt}] / [\text{base}]$$

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14. (a) With a neat sketch describe the components of a nuclear reactor.



1. The core of the nuclear reactor consists of uranium (^{235}U) in the form of cylindrical rods. These rods are dipped inside a liquid which is the moderator.
2. Whenever one neutron strikes this uranium rod nuclear fission reaction starts and 3 fast moving neutrons are produced.
3. Because of the moderator these 3 neutrons undergo elastic collision as a result they slow down before they strike the second rod.
4. Geometry of the core is such that only one out of 3 neutrons which are emitted strike the next rod making the reaction a controlled one.
5. When the control rods are inserted inside they will absorb all the extra neutrons. Since there are no neutrons nuclear fission reaction will stop.
6. Large amount of energy is also released in the core.
7. In order to extract the energy from the core water at very high pressure is passed through it.
8. As hot water passes through it produces steam in the steam generators.
9. This steam is used to run the turbines which in turn produce electricity.
10. This process will keep on continuing till the uranium on the rods does not get over. Then the rods have to be replaced in the nuclear reactor.

(OR)

(b) List down the properties of α , β , γ radiations:

ALPHA RAYS

- (1) **Nature:** They consist of streams of α -particles. By measurement of their e/m , Rutherford showed that they have a mass of 4 amu and charge of +2. They are helium nuclei and may be represented as $^4_2\alpha$ or ^4_2He .
- (2) **Velocity:** α -particles are ejected from radioactive nuclei with very high velocity, about one-tenth that of light.



- (3) **Penetrating power:** Because of their charge and relatively large size, α -particles have very little power of penetration through matter. They are stopped by a sheet of paper, 0.01 mm thick aluminium foil or a few centimetres of air.
- (4) **Ionisation:** They cause intense ionisation of a gas through which they pass. On account of their high velocity and attraction for electrons, α -particles break away electrons from gas molecules and convert them to positive ions.

BETA RAYS

- (1) **Nature:** They are streams of β -particles emitted by the nucleus. From their deflection electric and magnetic fields, Becquerel showed that β -particles are identical with electrons. They have very small mass (1/1827 amu) and charge of -1 . A β -particle is symbolized as ${}^0_{-1}\beta$ or ${}^0_{-1}e$.
- (2) **Velocity:** They travel about 10 times faster than α -particles. Their velocity is about the same as of light.
- (3) **Penetrating power:** β -Particles are 100 times more penetrating in comparison to α -particles. This is so because they have higher velocity and negligible mass. β -particles can be stopped by about 1 cm thick sheet of aluminium or 1 m of air.
- (4) **Ionisation:** The ionisation produced by β -particles in a gas is about one-hundredth of that of α -particles. Though the velocity of β -particles is higher but the mass being smaller, their kinetic energy is much less than α -particles. Hence they are poor ionisers.

GAMMA RAYS

- (1) **Nature:** Unlike α and β -rays, they do not consist of particles of matter. γ -Rays are a form of electromagnetic radiation of shorter wavelength than X-rays. They could be thought of as high-energy photons released by the nucleus during α - or β -emissions. They have no mass or charge and may be symbolized as ${}^0_0\gamma$.
- (2) **Velocity:** Like all forms of electromagnetic radiation, γ -rays travel with the velocity of light.
- (3) **Ionisation:** Their ionising power is very weak in comparison to α - and β -particles. A γ -photon displaces an electron of the gas molecule to yield a positive ion. Since the chances of photon-electron collisions are small, γ -rays are weak ionisers.
- (4) **Penetrating power:** Because of their high velocity and non-material nature, γ -rays are most penetrating. They cannot be stopped even by a 5 cm thick sheet of lead or several metres thick layer of concrete.



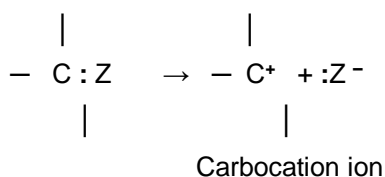
PART – C (2 X 10 =20)

Answer any TWO questions.

15. What are carbocations? Explain the relative stabilities of primary, Secondary and tertiary carbocations.

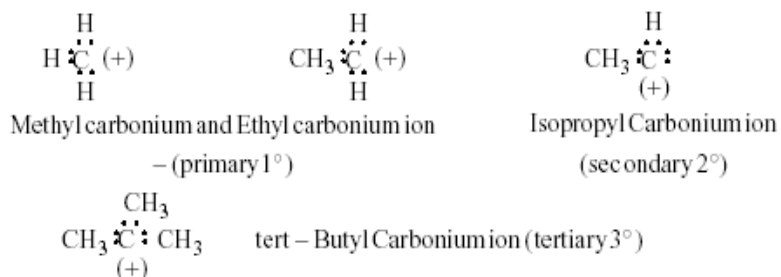
Carbonium ions(Carbocations): Organic ions which contains a positively charged carbon atom are called carboniumions or carbocations.

They are formed by heterolytic fission.



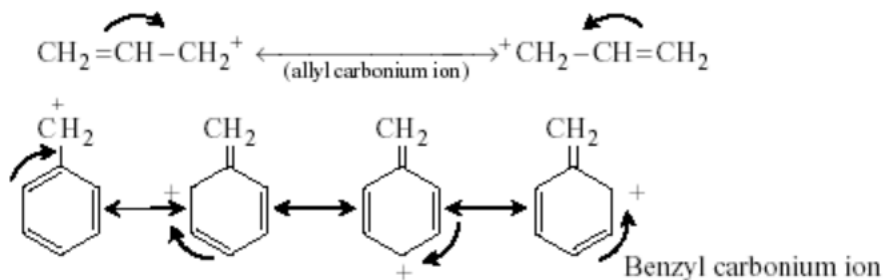
where Z is more electronegative atom than carbon.

Carbocation ions are named after the parent alkyl group and adding the words Carbocation ions. For example.

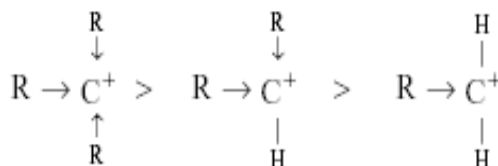


Stability of Carbocation Ions:

- The stability of Carbocation ion is influenced by both resonance and inductive effect.
- For example the allyl and benzyl Carbocation ions are much more stable than propyl Carbocation ions.
- Both allyl and benzyl Carbocation ions can be stabilised by resonance, but propyl Carbocation ion has no resonance forms.



- Electron releasing groups also stabilise Carbocation ions by partial neutralisation of the positive charge on carbon.
- Thus, a tertiary carbocation ion is more stable than a secondary which in turn is more stable than a primary because of the +I effect associated with alkyl groups



- Electron attracting groups (electrophiles) like 2NO^- , $-\text{Br}$ will make a carbocation ion less stable.

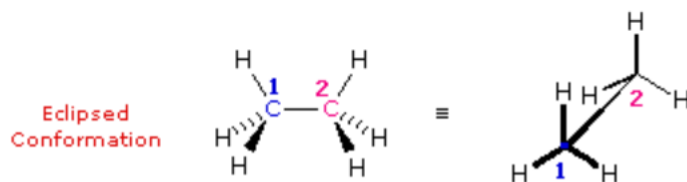
16. What are conformers? Discuss the various conformation of ethane with energy level diagram.

The different arrangements of the atoms in space the result from the rotation of groups about C - C bond axis are called Conformations or conformational Isomers.

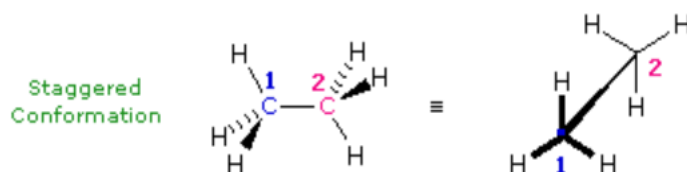
CONFORMATION OF ETHANE:

- The two tetrahedral methyl groups can rotate about the carbon – carbon bond axis yielding several arrangements called conformers.
- The extreme conformations are staggered and eclipsed conformation. There can be number of other arrangements between staggered and eclipsed forms and their arrangements are known as skew forms.

Eclipsed conformation: In this conformation, the hydrogen's of one carbon are directly behind those of the other. The repulsion between the atoms is maximum and it is the least stable conformer.

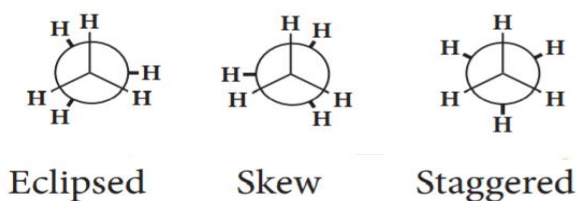


Staggered conformation: In this conformation, the hydrogen's of both the carbon atoms are far apart from each other. The repulsion between the atoms is minimum and it is the most stable conformer.



Skew Conformation: The infinite numbers of possible intermediate conformations between the two extreme conformations are referred as skew conformations.

The stabilities of various conformations of ethane are Staggered > Skew > Eclipsed

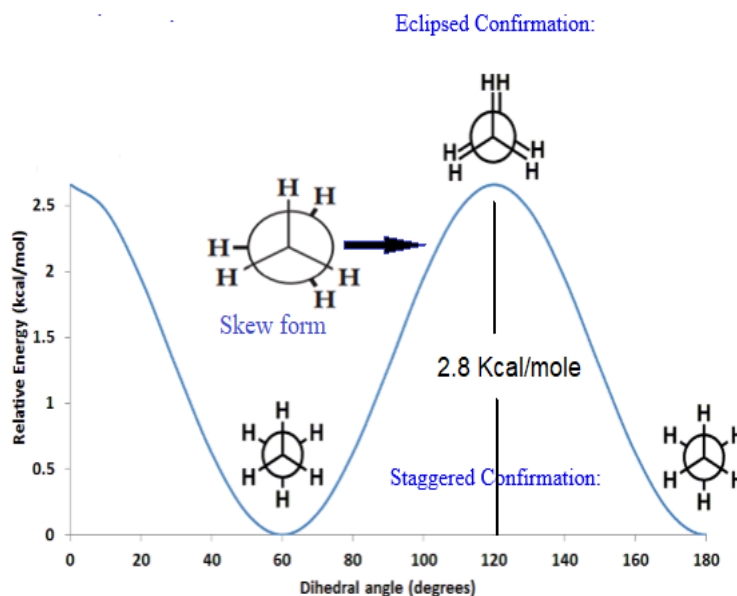


Eclipsed Skew Staggered

Newman Projection formula for ethane

The potential energy difference between the staggered and eclipsed conformation of ethane is around 12.5 KJmol⁻¹. The various conformations can be represented by new man projection formula.

The following potentially energy diagram shows the relative stabilities of various conformers of ethane.



17. What are buffer solutions? Explain the buffer action.

BUFFER SOLUTIONS

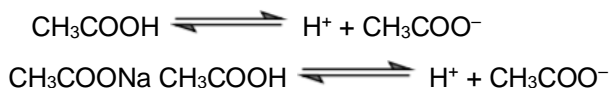
A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.

Two common types of buffer solutions are:

1. A weak acid together with a salt of the same acid with a strong base. These are called Acid buffers. (e.g.,) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.
2. A weak base and its salt with a strong acid. These are called Basic buffers. (e.g.) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

Buffer action:

Let us illustrate buffer action by taking example of a common buffer system consisting of a solution of acetic acid and sodium acetate ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$).



Since the salt is completely ionised, it provides the common ions CH_3COO^- in excess. The common ion effect suppresses the ionisation of acetic acid. This reduces the concentration of H^+ ions which means that pH of the solution is raised.

The pH of the buffer is governed by the equilibrium

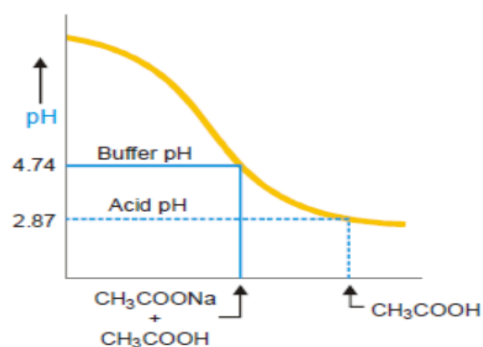




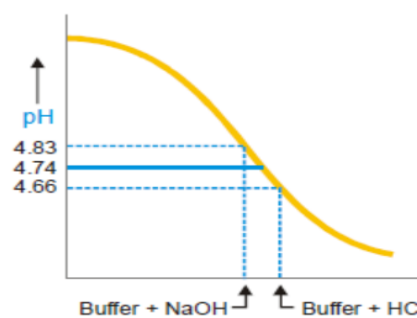
The buffer solution has a large excess of CH_3COO^- ions produced by complete ionisation of sodium acetate,



Buffer action with an example: Thus, a 0.1 M acetic acid solution has a pH of 2.87 but a solution of 0.1 M acetic acid and 0.1 M sodium acetate has a pH of 4.74 (as show in the figure). Thus 4.74 is the pH of the buffer. On addition of 0.01 mole NaOH the pH changes from 4.74 to 4.83, while on the addition of 0.01 mole HCl the pH changes from 4.74 to 4.66. Obviously the buffer solution maintains fairly constant pH and the changes in pH could be described as marginal.



The buffer solution ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) has a higher pH than the acid itself.



The pH of buffer changes only slightly upon addition of an acid (0.01 moles) or base (0.01 mole NaOH).

18. (a) Outline the principle of neutron activation analysis.

Neutron activation analysis is a nuclear method of elemental analysis in which the elements in a sample to be analyzed are made radioactive by irradiation with neutrons and the induced radioactive species are then identified and measured. The amount of a given neutron activation product that is formed during neutron irradiation is directly proportional to the amount of its parent isotope. Measurement of the radionuclide provides a measure of the total concentration of the parent element.

The basic equation for activation is

$$W = \frac{AM}{\sigma \phi (1 - e^{-\lambda t}) \times (6.02 \times 10^{23})}$$



where, W a weight of element irradiated, in grams

A = induced activity in disintegrations/sec at the end of irradiation

ϕ = flux of neutrons used in the irradiation, in neutrons/cm²/sec

σ = the activation cross section for the nuclear reaction concerned, in cm²

f = fractional abundance of the particular isotope of the element concerned

M = atomic weight of that element

λ = the decay constant of the induced radionuclide, in sec⁻¹

t = irradiation time, in seconds

(b) How are radio isotopes useful in the field of medicine, agriculture and industry?

- **Agriculture:** Plague control, food conservation, etc.
- **Art:** restoration of art objects, verification of historic or artistic objects, etc.
- **Archaeology:** Geological event dating, etc.
- **Research:** Universe, industry, medicine, etc.
- **Pharmacology:** The study of the metabolism of drugs before they are authorized for public use.
- **Industry and technology:** review of materials and welding in construction, control of productive processes, research, etc.
- **Medicine:** Diagnosis and treatment of diseases, sterilization of products frequently used in clinical and surgical environments, etc. Radioactive isotopes which are useful in medicine Isotope Use

S.No	ISOTOPES	USES
1	${}^3_1\text{H}$ Tritium	Measure water content of the body
2	${}^{11}_6\text{C}$ Carbon - 11	Brain scan
3	${}^{14}_6\text{C}$ Carbon - 14	Radio immunology
4	${}^{197}_{80}\text{Hg}$ Mercury - 197	Kidney scan
5	${}^{32}_{15}\text{P}$ Phosphorous-32	Detection of eye tumours
6	${}^{59}_{26}\text{Fe}$ Iron - 59	Diagnosis of anaemia
7	${}^{60}_{27}\text{Co}$ Cobalt – 60	Treatment of cancer



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B.Sc. DEGREE EXAMINATION,
NOVEMBER / DECEMBER 2018.
Third semester
Physics
Allied: CHEMISTRY –I
(COMMON FOR ALL BRANCHES)
(From 2017 -18 onwards)

Time: 3 hrs

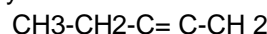
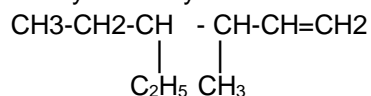
Maximum: 60 marks

PART A – (10 x 2 = 20)
Answer ALL the questions.

1. Write the structure formula of the following:

(a) 4-ethyl-3-methyl-1-hexene

(b) 2-pentyne



2. Write the IUPAC name of the following compounds:

(a) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3$

(b) $\text{CH}_3 - \text{CH}_2 - \underset{\text{Br}}{\text{CH}} - \underset{\text{Br}}{\text{CH}} - \text{CH}_3$

2-Pentene

2,3-dibromo pentane

3. What are the types of solution?

Depending upon the dissolution of the solute in the solvent, solutions can be categorized into supersaturated solution, unsaturated and saturated solutions.

- A **supersaturated solution** comprises a large amount of solute at a temperature wherein it will be reduced as a result the extra solute will crystallize quickly.
- An **unsaturated solution** is a solution in which a solvent is capable of dissolving any more solute at a given temperature.
- A **saturated solution** can be defined as a solution in which a solvent is not capable of dissolving any more solute at a given temperature.

4. Define the term pH.

It is defined as the negative of the base -10 logarithm (log) of the H^+ concentration. Mathematically it may be expressed as

$$\text{pH} = -\log_{10} [\text{H}^+],$$

where $[\text{H}^+]$ is the concentration of hydrogen ions in moles per litre.

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DATE : 04/09/2020
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PAGE 116 OF 135

Edition : 1

5. Define the term molarity, normality:

Molarity:

It is one of the most widely used units of concentration and is denoted by M. It is defined as no. of moles of solute present in 1 liter of solution. Thus,

Molarity = No. of moles of solute / Volume of solution (in Litres)

Normality:

The number of gram or mole equivalents of solute present in one litre of a solution.

Normality = No. of gram equivalents of solute / Volume of solutions (in litres)

6. Define the term Buffer solution with an example:

A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.

Two common types of buffer solutions are:

1. A weak acid together with a salt of the same acid with a strong base. These are called Acid buffers. (e.g.,) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.

2. A weak base and its salt with a strong acid. These are called Basic buffers. (e.g.) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

7. Define half-life period:

The time required to disintegrate one half of any radioactive substance is called half life period ($t_{1/2}$).

The half life period ($t_{1/2}$) of a radioactive substance is independent of initial concentration. It depends only on the disintegration constant (λ) of the radioactive element.

$$\left(t_{1/2} = \frac{0.693}{\lambda} \right)$$

$$\text{Average life, } \tau (\text{Tau}) = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

8. What are polysaccharides? Give example:

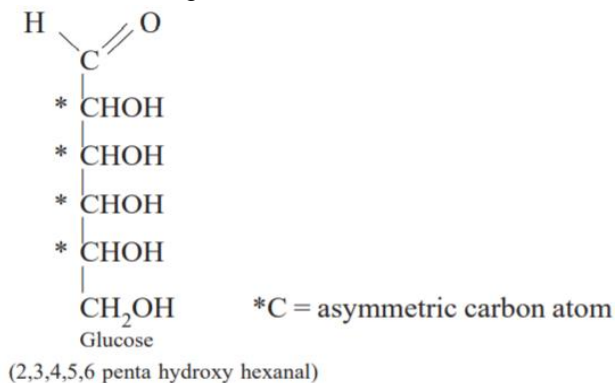
Example: starch, cellulose and glycogen (homopolysaccharides); hyaluronic acid and heparin (heteropolysaccharides).

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9. Draw the structure of glucose:



10. Give the test for sugars:

If there is reducing sugar then test solution is positive test will result in a precipitate the colour of which depends on the concentration of reducing sugar.

- a) Green – very low concentration
- b) Yellow – low concentration
- c) Orange - brown – medium concentration

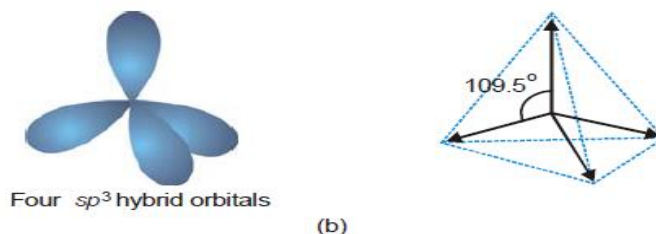
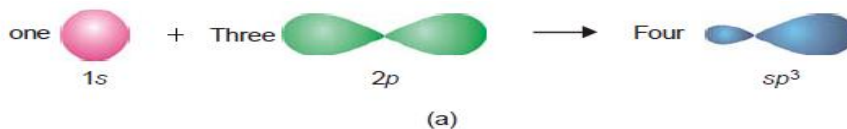
PART B – (4 X 5 = 20 MARKS)

Answer ALL the questions, choosing either (a) or (b)

11. (a) Explain sp^3 hybridization with an example.

sp^3 Hybridization:

- When one 's' orbital and 3 'p' of an atom mix together to form four new equivalent orbital, this type of hybridization is sp^3 . The new orbitals formed are called **sp^3 hybrid orbitals**.
- These are directed towards the four corners of a regular tetrahedron and make an angle of $109^\circ 28'$ with one another.
- The angle between the sp^3 hybrid orbitals is 109.28°
- Each sp^3 hybrid orbital has 25% s character and 75% p character.



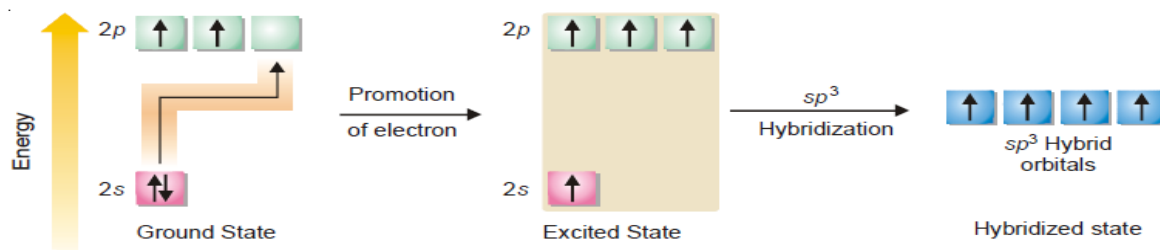
(a) sp^3 Hybridization (b) The four hybrid orbitals are directed towards the four corners of a tetrahedron and are at an angle of 109.5° to one another.

Example of sp^3 hybridization:

- methane (CH_4), ethane (C_2H_6)

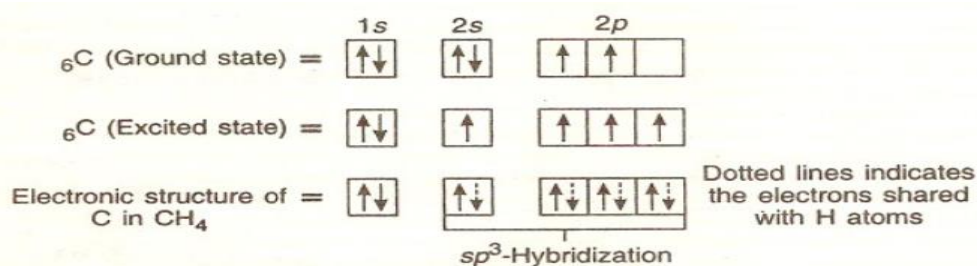
sp^3 Hybridization of Carbon

- The paired electrons in the 2s orbital of carbon is promoted to its $2p_z$ orbital in the excited state.
- The one 2s orbital and three 2p orbital of carbon mixes to give four equivalent sp^3 hybridised orbitals.



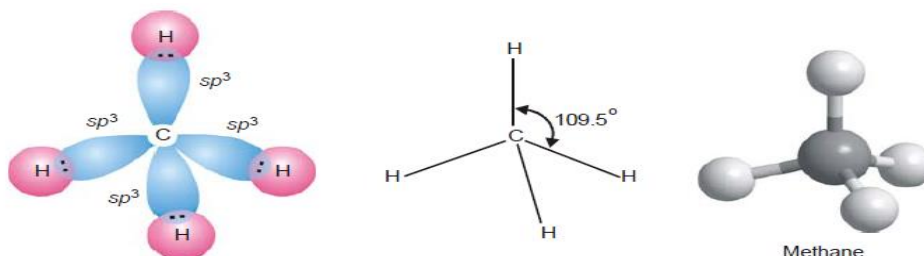
Various states of carbon atom; the orbitals here are undergoing sp^3 hybridization.

Formation of Methane molecule:





- The 1s orbitals of the four hydrogen atoms overlap linearly with the four sp^3 hybridised orbitals of carbon to form four C-H σ -bonds in the methane molecule.
- The symmetrical tetrahedral shaped CH_4 molecule is formed as shown below.



Shape and formation of methane molecule.

(OR)

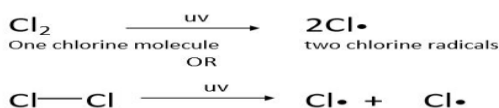
(b) Write a note on Homolytic and Heterolytic fission in organic compounds.

Homolytic fission:

In this process each of the atoms acquires one of the bonding electrons .



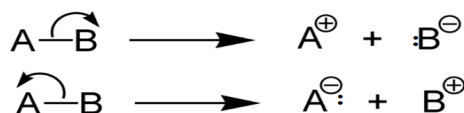
Example:



- The products, A and B are called Free Radicals.
- They are electrically neutral and have odd electron with them.
- Free radicals are highly reactive because of its odd electron which readily tends to get paired.
- Homolytic fission takes place mostly in vapour phase

Heterolytic fission:

In this process one of the atoms acquires both the bonding electrons when the bond is broken.



Example:



- The products of heterolytic fission are ions.
- Reactions which involve heterolytic fission take place at measurable rates.
- It occurs most readily with polar compounds in polar solvents.



(a) Explain: Dipole moment in organic molecules.

The dipole moment (μ) is the product of the magnitude of the charges and the distance between the charges.

Dipole Moment = Charge x Distance

$\mu = Q * R$ where, Q=charge & R= Distance between the two bonds

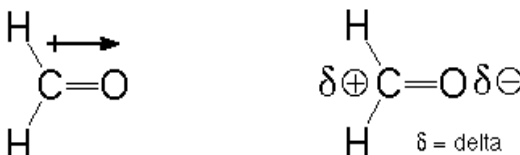
Note: i) Greater the charge larger will be the dipole moment

ii) Smaller is the distance lesser will be the dipole moment

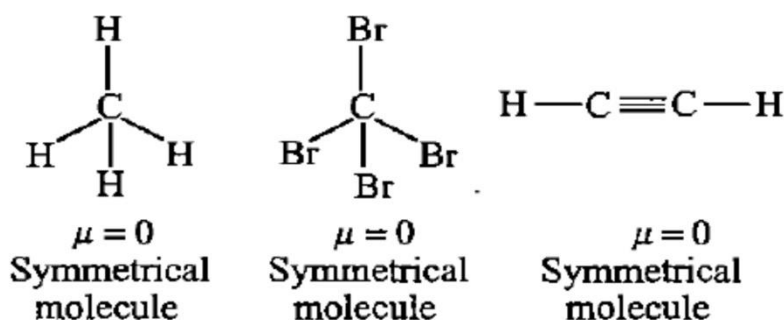
Some examples of dipole moment in organic molecules are give below:

The charge separation due to the difference in electronegativity and formation of partial positive and partial negative is called bond dipole. A chemical bond with charge separation due to difference in electronegativity is a polar covalent bond.

In Formaldehyde oxygen is more electronegative than carbon so Carbon –oxygen bond as a polarity. Oxygen has a partial negative charge and carbon has a partial positive charge and bond is dipole.



Symmetrical molecules are mostly have net dipole moment is zero. Some examples are given below:



(OR)

(b) Write note on Hydrogen bonding:

HYDROGEN BONDING:

- An electrostatic attractive force between the covalent bonded H- atom of one molecule and an electronegative atom (such as F, O, N) of other molecule.
- The size of electronegative atom should be small.



- Usually a hydrogen bond is represented by Dotted lines (----)
- Covalent bond is represented by Solid lines(———)



For Example : F—H ----- F—H

- H bond is a weaker as compare to a covalent bond.
- H bond energy is only 5-10 kcal/mol, as compared to the covalent bond energy of 50-100 kcal/mol but it is greater than Vander Waals attraction which is < 1 kcal/mole.

Conditions for H- Bonding:

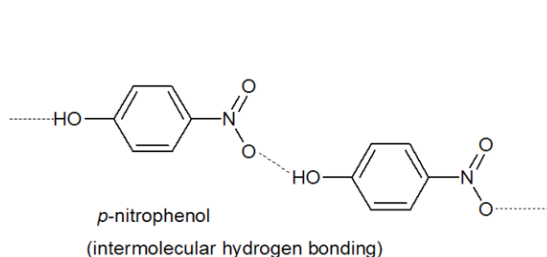
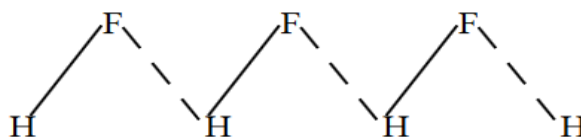
- High electronegativity of the atom bonded to hydrogen atom so that bond is sufficiently polar.
- Small size of the atom bonded to hydrogen so that it is able to attract the bonding electron pair effectively
- If the atom bonded to hydrogen has low value of electronegativity and/or large atomic size, dipole-dipole interactions are not strong enough to allow effective hydrogen bonding.

Types of hydrogen bonding:

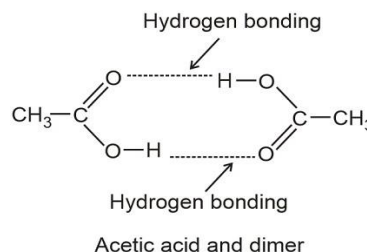
There are two types of hydrogen bonding (i) Intermolecular H-bonding (ii) Intramolecular H-bonding

(i) Intermolecular H-bonding: This type of bonding is between two or more same or different molecules when combine together to form a dimer or polymer respectively and leads to a phenomenon called association.

In the solid state, hydrogen fluoride consists of long zig-zag chains of molecules associated by hydrogen bonds as shown below: Therefore, hydrogen fluoride is represented as (HF)_n



Intermolecular hydrogen bonding in
p-nitrophenol



Dimeric structure of acetic acid

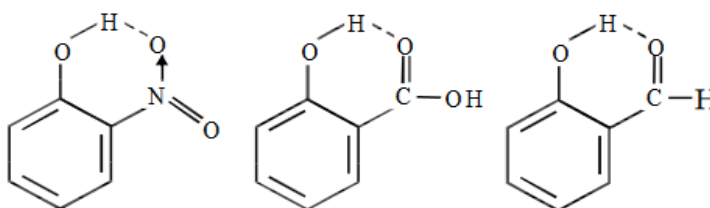


Intermolecular Hydrogen bonding increases the boiling points of the compound and also its solubility in water.

Intramolecular Hydrogen bonding:

- This type of bonding occurs within two atoms of the same molecule and leads to a phenomenon called Chelation.
- This type of hydrogen bonding frequently occurs in organic compound and result in the Cyclisation (six or five member ring) of the molecule.

Example for intramolecular Hydrogen bonding:



O-Nitro phenol

Salicylic acid

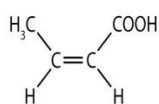
Salicylaldehyde

- This type of Hydrogen boiling decreases the boiling point of the compound and also its solubility in water.
- The large acidity is due to the intramolecular H- bonding which is capable of stabilising the salicylate ion.
- Intramolecular H-bonding is weaker than intermolecular H-bonding.

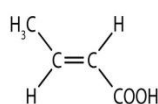
13. (a) Explain geometrical isomerism in organic compounds

Isomerism that arises out of difference in the spatial arrangement of atoms or groups about the doubly bonded carbon atoms is called Geometrical isomerism.

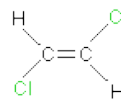
- Rotation about C=C is not possible at normal conditions and hence the isomers are isolable.
- This restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes.
- If different atoms or groups are bonded to the 'C=C' bond in a molecule, more than one spatial arrangement is possible. Few examples are shown below which exists in two isomeric forms.



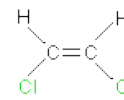
cis



trans



trans-1,2-dichloroethene



cis-1,2-dichloroethene

Cis –trans form of Butanoic acid

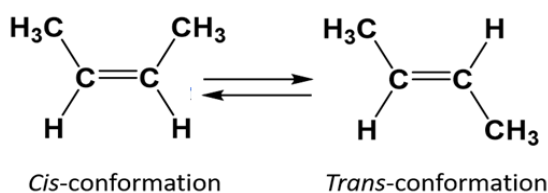
- These two compounds are referred to as geometrical isomers and are distinguished from each other by the terms *cis* and *trans*.



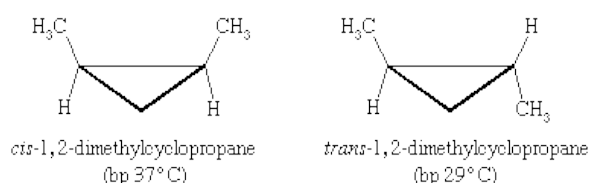
(i) *cis* – The *cis* isomer is one in which two similar groups are on the same side of the double bond.

(ii) *trans* - The *trans* isomer is one in which two similar groups are on the opposite side of the double bond.

- The *trans* isomer is more stable than *cis* isomer, because the bulky groups present on the same side do sue to steric hindrance *cis* less stable
- The conversion of *cis*-isomer into *trans*-isomer or vice versa (interconvert able) is possible when heated or absorbs light.

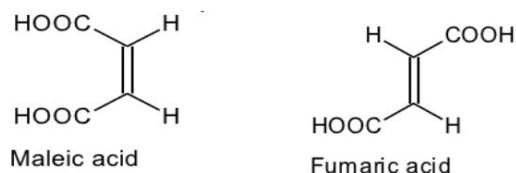


- Geometrical isomerism is possible in cyclic compounds also.
- There is restriction of rotation if two carbons are linked with cyclic structure.



Geometrical isomerism in Fumaric and Maleic acid:

- *Cis* and *trans* form of But-2-ene dioic acid is maleic acid and fumaric acid.
- *Tans* -isomer has greater symmetry than the *cis*- therefore *trans* has higher melting point.



- The maleic acid has m.p.130 ° C and fumaric acid has m.p. 300° C

(OR)

(b) Define the term Enantiomer and meso compounds

The non-super imposable mirror image forms a chiral molecules are called enantiomers.(optical isomers that are mirror images)

Characteristic features of Enantiomers:



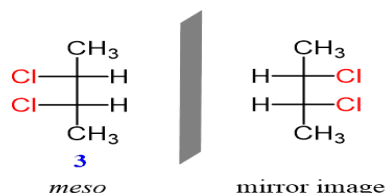
- Enantiomers have the same physical properties (bp ,mp, Density, solubility, etc..)
- Enantiomers will rotate plane polarized light the same magnitude (α) but opposite directions (+ or -).
- A mixture of equal amounts of two enantiomers is called a racemic mixture (optically inactive). A racemic mixture is a 50:50 mixture of two enantiomers.
- It cannot be interconverted under ordinary conditions.
- They have different biological properties .E.g. (+) - dextrose plays an important role in animal metabolism, whereas (-)-dextrose is not metabolized.
- A well know example is two isomers of Lactic acid (+ & -).

MESO COMPOUND

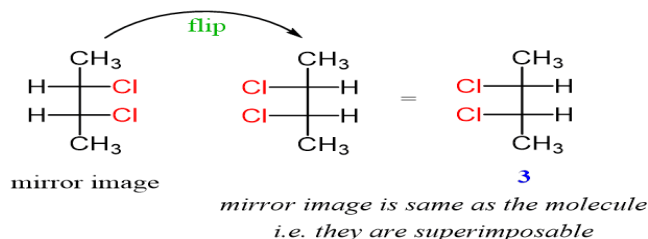
- Meso compound is a molecule with multiple stereocentres that is superimposable on its mirror image.
- Meso compounds are achiral compounds that have multiple chiral centres.
- Meso compounds are optically inactive.
- It has an internal symmetry plane that divides the compound in half.

Meso compounds do not have enantiomers!

Step 1. Draw the mirror image



Step 2. Flip the mirror image - it is the same compound



14. (a) Explain the concepts of acid and bases.

ACID AND BASE:

Three concepts of acids and bases are:

- Arrhenius concept
- Bronsted-Lowry concept

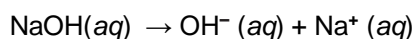
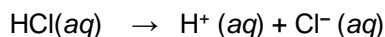


(c) Lewis concept

ARRHENIUS CONCEPT:

According to this concept, an acid is a compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.

For example, HCl is an Arrhenius acid and NaOH is an Arrhenius base.



Limitations of Arrhenius Concept

- (1) Free H^+ and OH^- ions do not exist in water.
- (2) Limited to water only.
- (3) Some bases do not contain OH^- .

BRONSTED-LOWRY CONCEPT

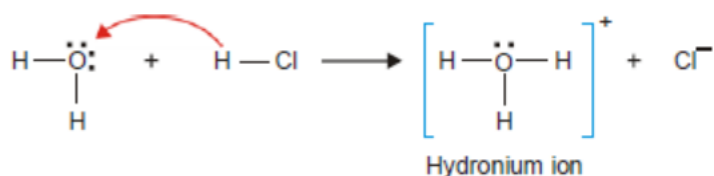
- An acid is any molecule or ion that can donate a proton (H^+)
- A base is any molecule or ion that can accept a proton

An acid qualifying Bronsted-Lowry concept is termed a Bronsted-Lowry acid or simply Bronsted acid.

A base qualifying Bronsted-Lowry concept is termed a Bronsted-Lowry base or simply Bronsted base.

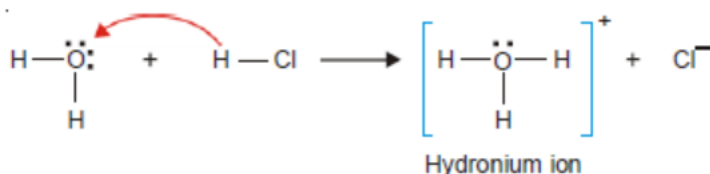
Examples of Bronsted acids and bases

(1) HCl gas and H_2O . When dry HCl gas dissolves in water, each HCl molecule donates a proton to a water molecule to produce hydronium ion.



Thus HCl gas is a Bronsted acid and water that accepts a proton is a Bronsted base.

(2) HCl and Ammonia, NH_3 . HCl gas reacts with ammonia (NH_3) to form solid NH_4Cl .



HCl is a proton donor and hence a Bronsted acid, while NH_3 is a proton acceptor and a Bronsted base.



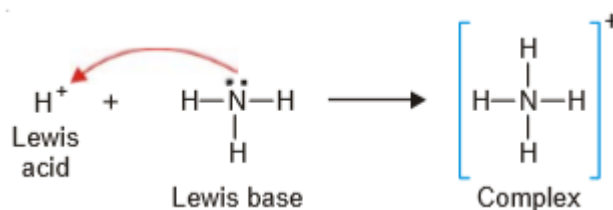
Lewis concept

A Lewis acid is a positive ion (or) an electron deficient molecule and a Lewis base is an anion (or) neutral molecule with at least one lone pair of electrons.

According to Lewis theory, an acid is an electron-pair acceptor a base is an electron-pair donor. All cations or molecules short of an electron-pair act as Lewis acids and all anions or molecules having a lone electron-pair act as Lewis bases.

Examples of Lewis reactions

Between H^+ and NH_3 , Proton (H^+) is a Lewis acid as it can accept an electron-pair. Ammonia molecule ($:NH_3$) has an electron-pair which it can donate and is a Lewis base. Thus the Lewis reaction between H^+ and NH_3 can be written as:



(OR)

- Derive Henderson equation:

HENDERSON EQUATION:

The pH of an acid buffer can be calculated from the dissociation constant, K_a , of the weak acid and the concentrations of the acid and the salt used.

The dissociation expression of the weak acid, HA, may be represented as



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

$$\text{Or } [H^+] = \frac{[HA] K_a}{[A^-]} \quad \dots (1)$$

The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt ($Na^+ A^-$) which provides A^- ions (Common ion effect). As a result the equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration $[A^-]$ is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus we can write the equation (1) as



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REV. NO. : R0
DATE : 04/09/2020
COPY :
PAGE 116 OF 135

Edition : 1

$$[H^+] = K_a \times [\text{acid}] / [\text{salt}] \quad \dots (2)$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used. Taking negative logs of both sides of the equation (2), we have

$$-\log [H^+] = -\log K_a - \log [\text{acid}] / [\text{salt}] \quad \dots (3)$$

$$-\log [H^+] = \text{pH} \text{ and } -\log K_a = \text{p}K_a$$

Thus from (3) we have

$$\text{pH} = \text{p}K_a - \log [\text{acid}] / [\text{salt}]$$

$$= \text{p}K_a + \log [\text{salt}] / [\text{acid}]$$

$$\text{Hence, pH} = \text{p}K_a + \log [\text{salt}] / [\text{acid}]$$

This relationship is called the Henderson-Hasselbalch equation or simply Henderson equation.

In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as :

$$\text{pOH} = \text{p}K_b + \log [\text{salt}] / [\text{base}]$$

PART – C (2 X 10 =20)

Answer any TWO questions.

15. Write a brief note on conformational analysis of cyclohexane.

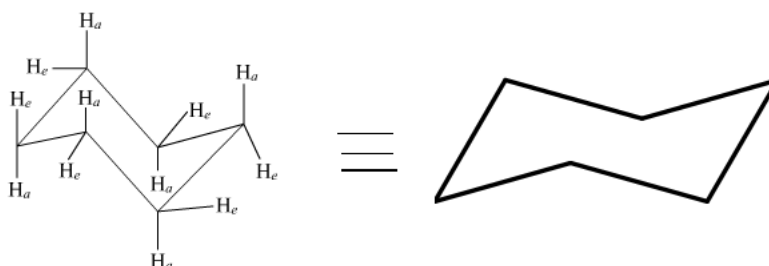
CONFORMATION OF CYCLOHEXANE:

The Chair conformation is the most stable conformation of cyclohexane. In chair cyclohexane there are two types of positions, axial and equatorial. The axial positions point perpendicular to the ring and equatorial positions are around the plane of the ring.

The less stable conformer is the *boat* conformation. This too is almost free of angle strain, but in contrast has torsional strain associated with eclipsed bonds at the four of the C atoms that form the side of the boat.

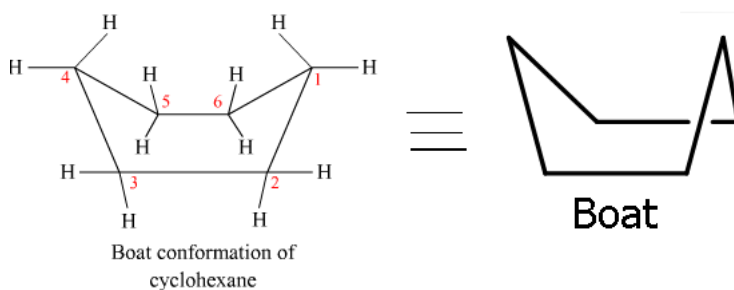
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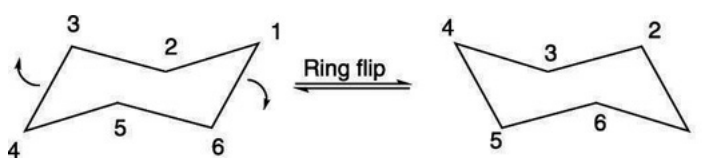


Chair conformation of cyclohexane
Six axial (*a*) and six equatorial (*e*)
hydrogen atoms.

Boat is twisted to give the *twist* or *skew-boat* conformation. The twist relieves some of the torsional strain of the boat and moves the flagpole H further apart reducing the steric strain. Consequently the twist boat is slightly more stable than the boat.



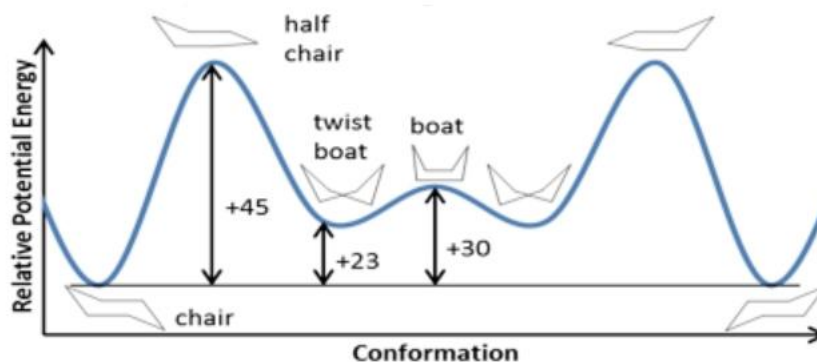
Conformational rotation of cyclohexane interconverts the conformations. This proceeds from one chair to twist boat to boat to twist boat to the other chair conformation. This process is often referred to as "**ring flipping**".



The potential energy
Cyclohexane is

Boat form is formed as an intermediate during the ring flip

difference in conformation of
shown below:



The energy difference shows that the chair conformation has the lowest energy and the boat form and half chair conformation are in the highest energy. It has been calculated that 99.9% of cyclohexane molecules are in the chair form at any time.

16. (a) Write note on Physiological buffer

PHYSIOLOGICAL BUFFERS

Physiological buffers are chemicals used by the body to prevent large changes in the pH of a bodily fluid.

The four physiological buffers are the bicarbonate, phosphate, hemoglobin, and protein systems.

Explanation:

The pH of a buffer is determined by the Henderson-Hasselbalch equation:

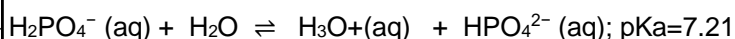
$$\text{pH} = \text{p}K_a + \log\left(\frac{A^-}{HA}\right)$$

The buffer is best able to resist changes in pH when the pH of the buffer is close to the pH of blood (7.37 to 7.42), so the pKa of the acid should be close to 7.4.

Phosphate Buffer

The phosphate buffer system consists of H_2PO_4^- and HPO_4^{2-} ions.

The equilibrium is



The phosphate buffer can easily maintain a pH of 7.4.

Carbonate Buffer

The equilibrium is



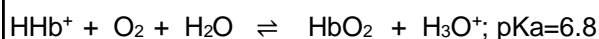


This buffer functions in exactly the same way as the phosphate buffer, but it is not ideal because its pKa is too far from pH 7.4.

Perhaps more importantly, the enzyme *carbonic anhydrase* converts H_2CO_3 into CO_2 that is dissolved in the blood and is then exhaled as CO_2 gas.

Hemoglobin

The general equation is:



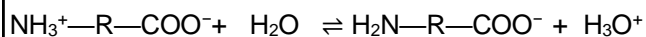
It shows that oxygenation of Hb promotes the formation of H_3O^+ .

This shifts the bicarbonate buffer equilibrium towards CO_2 formation, and CO_2 is released from the red blood cells.

Proteins

A protein is a long chain of amino acid residues, but this long chain still has free carboxylate groups COO^- and free amino groups NH_2 .

We could write the equation for a protein buffer system as

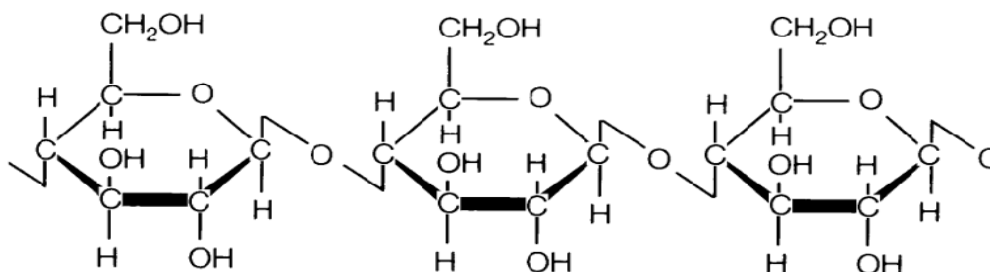


The protein can then act as a buffer.

12. Write short note on cellulose:

CELLULOSE:

Cellulose is the major constituent of plant cell walls. Cotton is almost pure cellulose. On hydrolysis cellulose yields D-glucose molecules. Cellulose is a straight chain polysaccharide. The glucose molecules are linked by β (1, 4) glycosidic bond.



Structure of Cellulose

Uses:

1. Cellulose is used extensively in the manufacturing paper, cellulose fibres, rayon explosive, (Gun cotton – Nitrated ester of cellulose) and so on.

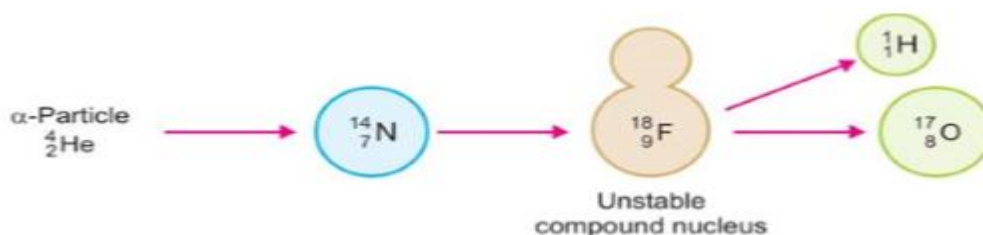


2. Human cannot use cellulose as food because our digestive systems do not contain the necessary enzymes (glycosidase or cellulases) that can hydrolyse the cellulose.

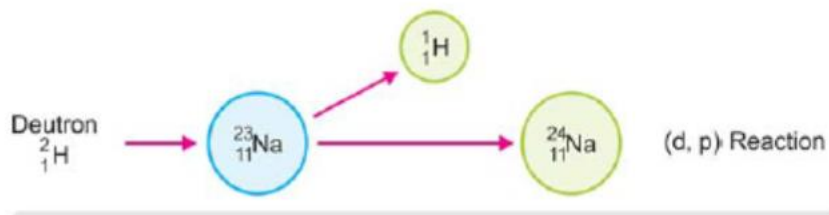
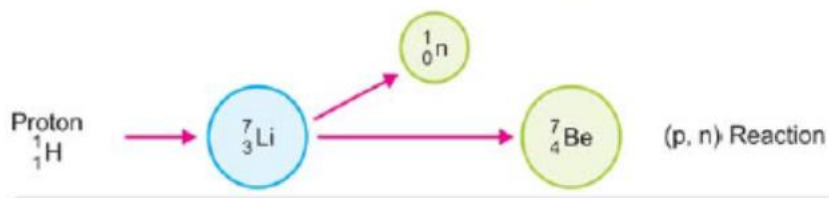
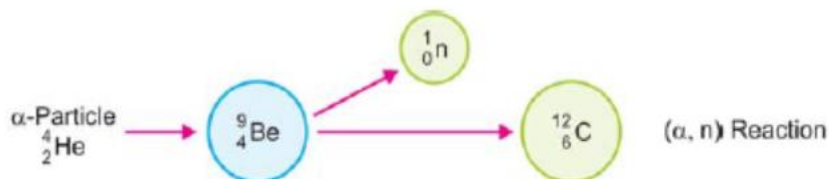
17. (a) Write a brief account on nuclear reaction:

NUCLEAR FISSION REACTIONS

In these reactions an atomic nucleus is broken or fissioned into two or more fragments. This is accomplished by bombarding an atom by alpha particles (${}^4_2\text{He}$), neutrons (${}^1_0\text{n}$), protons (${}^1_1\text{H}$), deuterons (${}^2_1\text{H}$), etc. This does not apply to neutrons which are electrically neutral. The projectile enters the nucleus and produces an unstable 'compound nucleus'. It decomposes instantaneously to give the products. For example, ${}^{14}_7\text{N}$ when struck by a α -particle first forms an intermediate unstable compound nucleus, ${}^{18}_9\text{F}$, which at once cleaves to form stables ${}^{17}_8\text{O}$.



Other examples are,

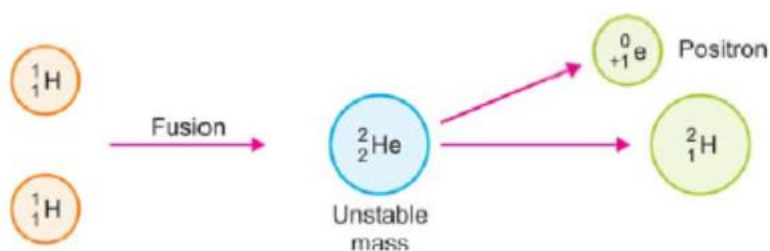




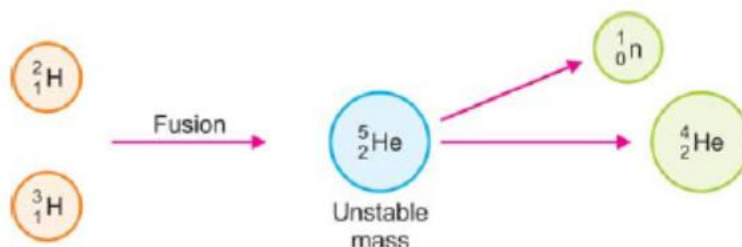
NUCLEAR FUSION REACTIONS

These reactions take place by combination or fusion of two small nuclei into a larger nucleus. At extremely high temperatures the kinetic energy of these nuclei overweighs the electrical repulsions between them. Thus they coalesce to give an unstable mass which decomposes to give a stable large nucleus and a small particle as proton, neutron, positron, etc. For example: Two hydrogen nuclei, ${}^1_1\text{H}$, fuse to produce a deuterium nucleus, ${}^2_1\text{H}$.

(1) Two hydrogen nuclei, ${}^1_1\text{H}$, fuse to produce a deuterium nucleus, ${}^2_1\text{H}$.

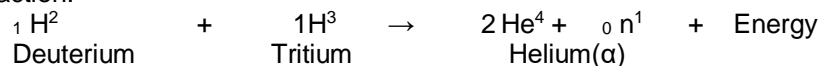


(2) Deuterium nucleus, ${}^2_1\text{H}$, and tritium nucleus, ${}^3_1\text{H}$, combine to give helium nucleus, ${}^4_2\text{He}$ with the expulsion of a neutron.



(b) How are α -rays produce? Mention its properties

Nuclear fusion reaction takes place at very high temperature of about 108 K. Therefore, this reaction is called thermonuclear reaction.



PROPERTIES OF ALPHA RAYS

- Nature:** They consist of streams of α -particles. By measurement of their e/m , Rutherford showed that they have a mass of 4 amu and charge of +2. They are helium nuclei and may be represented as ${}^4_2\alpha$ or ${}^4_2\text{He}$.
- Velocity:** α -particles are ejected from radioactive nuclei with very high velocity, about one-tenth that of light.



- (3) **Penetrating power:** Because of their charge and relatively large size, α -particles have very little power of penetration through matter. They are stopped by a sheet of paper, 0.01 mm thick aluminium foil or a few centimetres of air.
- (4) **Ionisation:** They cause intense ionisation of a gas through which they pass. On account of their high velocity and attraction for electrons, α -particles break away electrons from gas molecules and convert them to positive ions.

18. (a) Give an account on application of Radioactive isotopes in Agriculture and medicine:

Applications of radioisotopes

- **Medicine:** Diagnosis and treatment of diseases, sterilization of products frequently used in clinical and surgical environments, etc.
- **Industry and technology:** review of materials and welding in construction, control of productive processes, research, etc.
- **Agriculture:** Plague control, food conservation, etc.
- **Art:** restoration of art objects, verification of historic or artistic objects, etc.
- **Archaeology:** Geological event dating, etc.
- **Research:** Universe, industry, medicine, etc.
- **Pharmacology:** The study of the metabolism of drugs before they are authorized for public use.

Radioactive isotopes which are useful in medicine Isotope Use

ISOTOPES	SYMBOL	USES
Tritium	${}_1\text{H}^3$	Measure water content of the body
Carbon - 11	${}_6\text{C}^{11}$	Brain scan
Carbon - 14	${}_6\text{C}^{14}$	Radio immunology
Iodine – 131	${}_{53}\text{I}^{131}$	Diagnosis of damaged heart muscles and hyper thyroidism
Mercury - 197	${}_{80}\text{Hg}^{197}$	Kidney scan
Phosphorous-32	${}_{15}\text{P}^{32}$	Detection of eye tumours
Iron - 59	${}_{26}\text{Fe}^{59}$	Diagnosis of anaemia
Cobalt – 60	${}_{27}\text{Co}^{60}$	Treatment of cancer

(b) Write a note on mutarotation with an example:



MUTAROTATION:

- When D-glucose is crystallized at room temperature and a fresh solution is prepared, its specific rotation of polarised light is 112° ; but after 12 -18 hrs it changes to $+52.5^\circ$
- This change in rotation with time is called as mutarotation.
- Glucose has two anomers α and β .

