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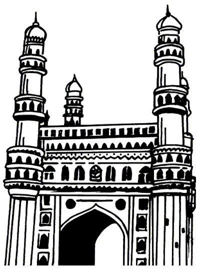

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UNIT - I

(Inorganic Chemistry)

S4-I-1: Coordination Compounds –II

Crystal field theory (CFT) - Postulates of CFT, splitting patterns of d - orbitals in O ctahedral, tetrahedral, square planer with suitable examples. Crystalfield stabilization energies and its calculations for various dn configurations in octahedral complexes. High Spin Low Spin complexes. Colour and Magnetic properties of transition metal complexes. Calculations of magnetic moments spin only formula. Detection of complex formation-basic principles of various methods - change in chemical properties, solubility, colour, pH, conductivity, magnetic susceptibility.

Hard and soft acids bases (HSAB) - Classification, Pearson's concept of hardness and softness, application of HSAB principles – Stability of compounds / complexes, predicting the feasibility of reaction. Thermodynamic and kinetic stability of transition of metal complexes. Stability of metal complexes – stepwise and overall stability constant and their relationship and chelate effect determination of composition of complex by Job's method and mole ratio method.

Applications of coordination compounds: Applications of coordination compounds a) in quantitative and qualitative analysis with suitable examples b) in medicine for removal of toxic metal ions and cancer therapy c) in industry as catalysts polymerization – Ziegler Natta catalyst d) water softening.

S4-I-2:Bioinorganic Chemistry

Essential elements, biological significance of Na, K, Mg, Ca, Fe, Co, Ni, Cu, Zn and chloride (Cl^-). Toxic metal ions As, Hg & Pb Oxygen transport and storage – structure of hemoglobin, binding and transport of oxygen. Fixation of CO_2 in photosynthesis - over view of light and dark reactions in photosynthesis. Structure of chlorophyll and coordination of magnesium. Electron transport in light reactions from water to $NADP^{\oplus}$ (Z – scheme).

S4-I-1: COORDINATION COMPOUNDS-II

Q1. Describe the postulates of CFT.

Ans : **(Imp.)**

Crystal Field Theory

To explain colour, magnetic properties and some other properties of crystalline substances, Bethe and vanvleck proposed and developed crystal field theory.

Postulates

- This theory considers the metal ion as being placed in an electrostatic field created by the ligand.
- This theory considers a complex as a combination of central ion surrounded by molecules with electric dipoles called as ligands. That means according to this theory ligands are considered as point dipoles (or) point charges.
- The bonding between metal cation and ligand arises due to electrostatic attraction between metal cation and ligand.
- The bond between the metal and ligand is considered as purely ionic.
- The repulsive forces arises between metal and ligand are responsible for splitting of d-orbitals.
- When a metal added in a ligand solution, all the ligands approach the metal ion in spherically symmetric geometry among the corners by this the energy of five d-orbitals increases but degeneracy is not lifted.
- In the second step the ligand try to approach towards the metal ion then it destroys degeneracy of a d orbitals during formation of complex.
- In presence of some ligands splitting occurs very less i.e., the energy difference between the d-orbitals is very less. Those ligands are known as weak field ligands.
- The presence of few ligands splitting occurs very large i.e., the energy difference between d-orbitals is very large, those are called strong field ligands.
- In presence of weak ligands pairing of e^-takes place according to Hund's rule of maximum multiplicity due to less energy difference between d-orbitals.
- In presence of strong field ligands due to large energy difference between d-orbitals, e^- pairing takes place in the lower energy d-orbitals itself, i.e., against Hund's rule.
- When the spin magnetic moment of metal atom decreases inpresence of ligand field then the resulting complex is known as low spin complex.
- If the spin magnetic moment remains same in the presence of ligand field then the resulting complex is known as high spin complex.

Q2. Explain the splitting pattern of d-orbitals in octahedral.

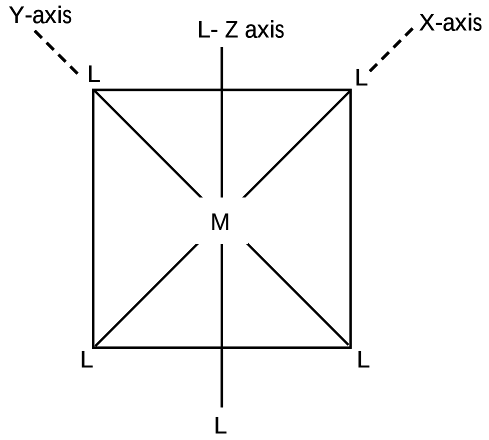
Ans :

d-Orbital Splitting in Octahedral Complexes

In an octahedral complexes, six ligands approach the metal along the axes x, y, z of the coordinate system. Among these 6 ligands, 2 approach along x-axis, 2 approach along y-axis and other two along z-axis.

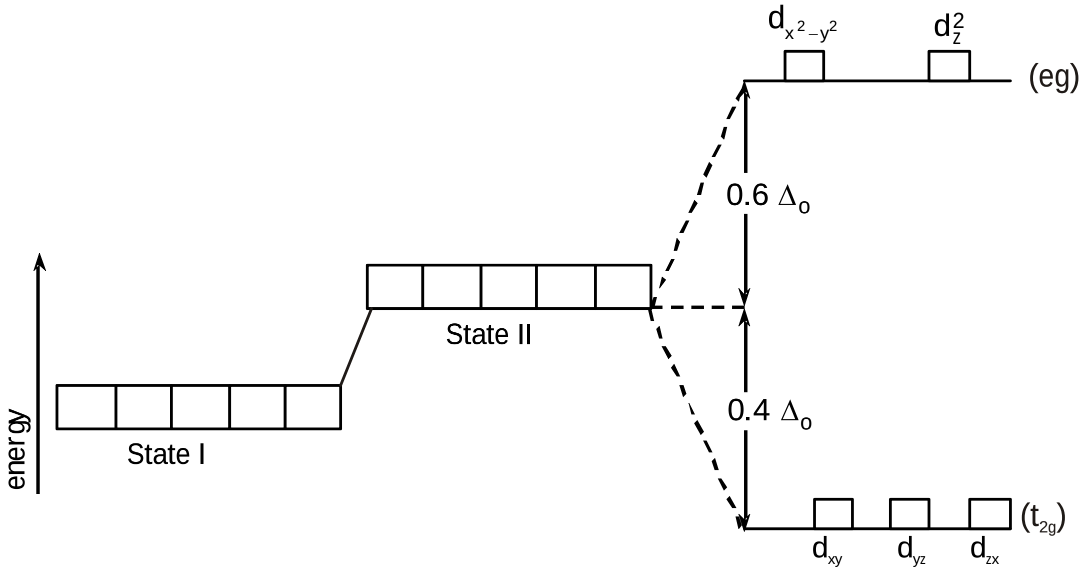
Since the ligands approach in this field along the axes the orbitals oriented along the axis i.e., $d_{x^2y^2}$ and d_{z^2} will be repelled more than the d-orbitals d_{xy}, d_{yz} and d_{zx}.

Consequently energy of two eg orbitals increases more than energy of three t_{2g} orbitals. Thus, the five d-orbitals split in two groups of different energies.



The approach of ligand is considered as a two step process in the first step, it is assumed that the ligands approach the metal ion spherically i.e., at an equal distance from each of orbitals at this stage all the d-orbitals are raised in energy by the same amount.

In the second step the spherical field ligand changes to the octahedral field leading to splitting of orbitals.



State I

It represents degeneracy of all the five d-orbitals of the free metal ion in the absence of ligands.

State II

It represents hypothetical degeneracy of all five d-orbitals at a higher energy level when all ligands approaching the central ion are at an equal distance from each of the d-orbitals.

State III

It represents splitting of d-orbitals in the octahedral crystal field.

The splitting of degenerate d-orbitals in different groups of orbitals of different energies under the influence of crystal field is called "crystal field splitting"

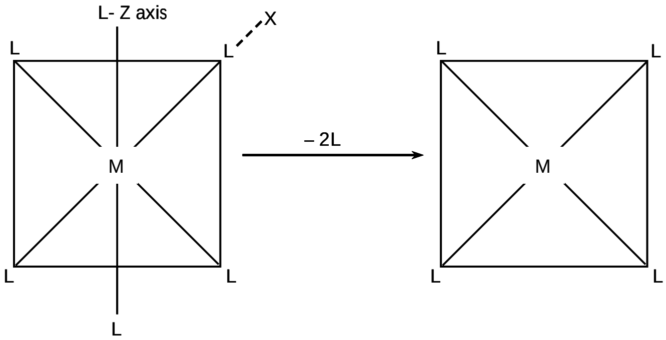
The difference in the energy levels of these two groups of d-orbitals arising as a result of d-orbital splitting is called "crystal field splitting energy". This energy difference is denoted Δ_0 [where subscript O indicates octahedral complex]. The extent of splitting depends upon the field strength of ligand.

Q3. Write the splitting pattern of d-orbitals in square planer complex.

Ans :

d-orbital Splitting in Square Planar Complex

Crystal field theory considered square planar complexes as the one derived from octahedral field by with drawing two trans ligands located along the z-axis.



By removing away the two ligands present on z-axis the d_z^2 orbital oriented along z-axis is completely from the repulsion by ligand orbitals.

In the similar way d_{xz}, d_{yz} orbitals having 'z' axis orientation reduce their repulsion by the ligands to some extent. The energy of these 'd' orbitals is reduced differently.

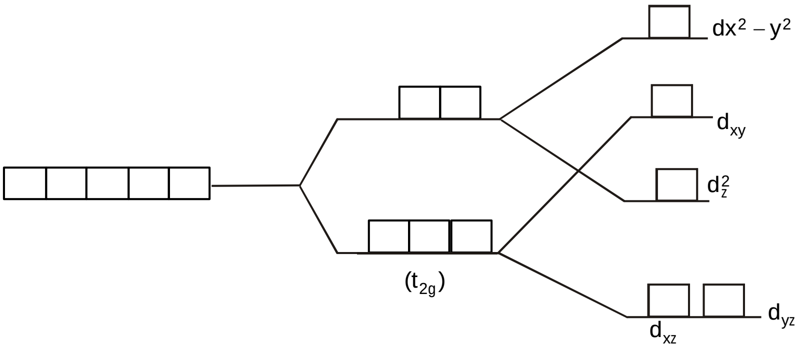
The energy of d_{z^2} orbital is highly reduced since this orbital is completely free from the repulsions by the ligand orbitals.

d_{xz}, d_{yz} orbitals being oriented in the space between xz, yz axes, there will be small repulsion between these orbitals and the orbitals of the ligands present on x and y axes.

Therefore the decrease in the energy of these orbitals is much less than the decreases in d_{z^2} orbitals.

The energy of $d_{x^2-y^2}$ oriented an x, y axes is very high since these orbitals are under high repulsion by the orbitals of the ligands present on x, y axes. The d_{xy} orbital which is oriented between the axes is under lesser repulsion by the ligand. Hence their energy is little higher. The crystal field splitting is shown by Δ_{sp}.

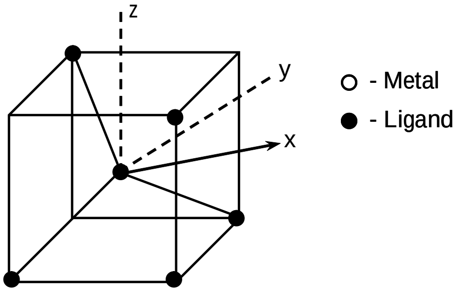
Crystal field splitting energy (Δ_{sp}) is more than (Δ_0 Δ_{SP} = 1.3 Δ_0).



Q4. Explain d-orbital splitting in Tetrahedral complexes.

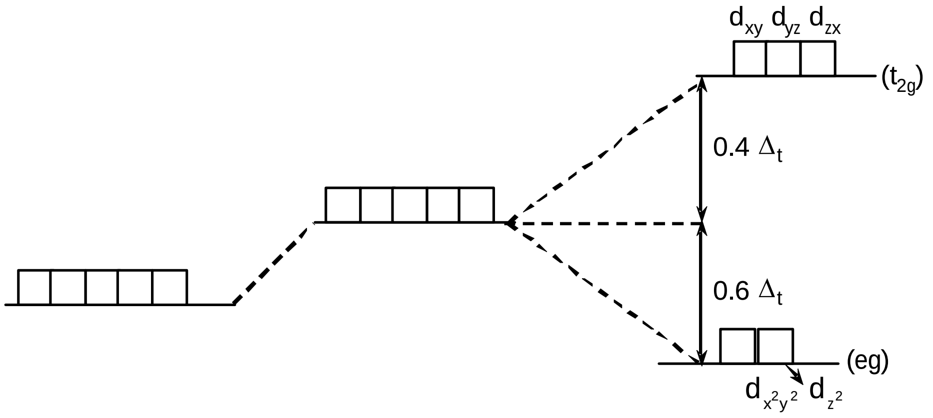
Ans :

d-Orbital Splitting in Tetrahedral Complexes



Coordination number in tetrahedral complexes is 4, In a tetrahedral field, the ligands approach in a different way i.e., ligands approach the central metal atom in between the areas thus ligands interact more with d_{xy}, d_{yz} and d_{zx} [t_{2g}] orbitals which are pointing close to the direction of approaching ligands whereas $d_{x^2y^2}$ d_{z^2} (eg) orbitals oriented along the axes are repelled to less extent.

Therefore energy of t_{2g} orbitals increases and energy of eg., orbitals decreases.



Δ_t is found less than Δ_0

$$\Delta_t = \frac{4}{9}\Delta_0.$$

Q5. Show the formulations of calculations for various d^n configurations in octahedral complexes.

Ans : **(Imp.)**

Low Spin - High Spin Complexes

In metal complexes the magnitude of crystal field splitting depends on the nature of the ligands forming the complex.

When some metal ion is complexed with different ligands Δ values are different.

The value of Δ depends upon the field.

Strength of the ligand Ligands which produce greater splitting are called strong ligands and intermediary splitting are called intermediary ligands.

The ligands are arranged in the increasing or decreasing order their field strength. This series is called spectrochemical series.

Low Spin Complex

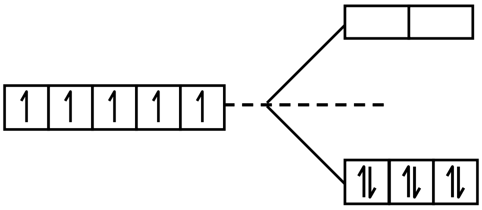
In presence of strong field ligands, d-orbitals are splitted to greater extent hence t_{2g} orbitals are paired first then the $e^{\ominus}$ enter into eg orbitals. That is pairing is taking against Hunds rules and the complex formed is known as low spin complex as magnetic moment of formed complex is less than the metal ion.

Example

$[Mn(CN)_6]^{-4}$

Oxidation state of Mn = +2

Electronic configuration of $Mn^{+2} = d^5s^0$



As CN^- is strong field ligand pairing taking place against Hund's rule and magnetic moment of complex is due to observe of unpaired $e^{\ominus}$ but metal ion showing magnetic behaviour.

High Spin Complex

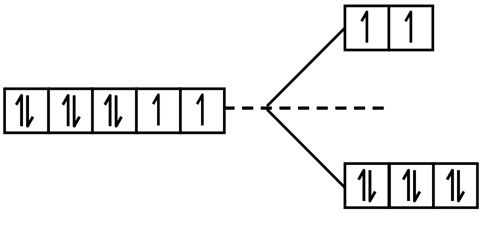
In the presence of weak field ligands pairing does not occur against the Hund's rule due to less energy difference between d-orbitals. If spin magnetic moment of complex remains some or they increased in the presence of ligand field then the resulting complex is known as high spin complex.

Ex: $[Ni(NH_3)_6]^{+2}$

Oxidation state for Ni = +2

Electronic configuration of $Ni^{+2} = d^8s^0$

NH_3 is weak field ligand



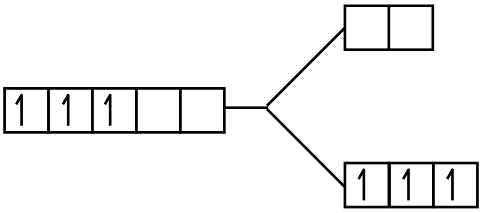
∴ Splitting occurs to less extent and number of unpaired $e^{\ominus}$s in metal ion and in presence of ligand field some. Therefore magnetic field also same. Hence high spin complex.

Ex: $[Cr(CN)_6]^{-3}$ Oxidation state for cr = + 3

Electronic configuration of $cr^{3+} = d^3s^o$

CN is a strong filed ligand

Though strong field ligand number of unpaired $e^{\ominus}$ same hence magnetic moment same high spin complex.



Q6. Explain Crystal Field Stabilization Energy with example.

Ans : **(Imp.)**

Crystal Field Stabilization Energy

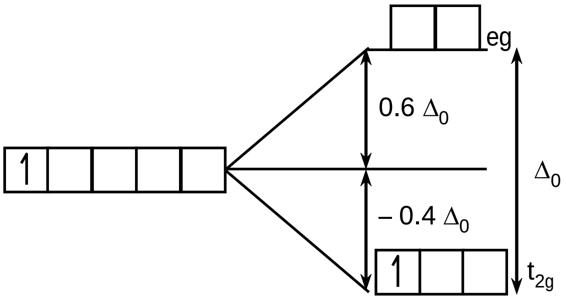
Under the influence of crystal field, the d-orbitals of the metal split into two energy levels (higher and lower energy levels) Therefore electrons enter selectively into lower energy d-orbitals. Thus the energy of the complex being formed is lowered, the complex attains stability. The energy is called crystal field stabilization energy (CFSE).

In $\left[Ti(H_2O)_6\right]^{+3}$ complex single $e^{\ominus}$ is present Ti^{+3}. In free metal ion all the 5d - orbitals are degenerate. Therefore this can enter any of these 5 d-orbitals.

But when Titanium i.e., Ti^{+3} forms a complex with $6H_2O$ d-orbitals are split into t_{2g} and eg orbitals have higher energy 0.6 Δ_0 single $e^{\ominus}$ of Ti^{+3} enters into t_{2g} where by energy decreases by 0.4 Δ_0. This 0.4 is CFSE.

Δ_0 (Energy difference between two d-orbitals) of $\left[Ti(H_2O)_6\right]^{+3}$ is 58.0 kCal/mole.

Thus CFSE is $0.4 \times 58 = 23.2$ kcal/mole. That means complex is more stable than free Ti^{+3} ion by 23.2 kcal/mole.



Calculation of CFSE

Octahedral complex = $[-0.4 + t_{2g}\ e^{\ominus}s + 0.6 \times eg\ e^{\ominus}]\Delta_0$

Tetrahedral complex = $[-0.6 \times eg\ e^{\ominus}s + 0.4 \times t_{2g}e^{\ominus}]\Delta t$

The electronic arrangement, CFCE values of octahedral.

No. of $e^{\ominus}$	Presence of weak field ligand		CFSF	Presence of strong field ligand		CFSE
	t_{2g}	eg		t_{2g}	eg	
1.	(↑)00	00	$-0.4\ \Delta_0$	(↑)00	00	$-\ 0.4\ \Delta$
2.	(↑)(↑)	00	$-0.8\ \Delta_0$	(↑)(↑)0	00	$-\ 0.8\ \Delta$
3.	(↑)(↑)(↑)	00	$-1.2\ \Delta_0$	(↑)(↑)(↑)	00	$-\ 1.2\ \Delta_0$
4.	(↑)(↑)(↑)	(↑)0	$-0.6\ \Delta_0$	(↑↓)(↑)(↑)	00	$-\ 1.6\ \Delta_0$
5.	(↑)(↑)(↑)	(↑)(↑)	0 0	(↑↓)(↑↓)(↑)	00	$-\ 2.0\ \Delta_0$
6.	(↑↓)(↑)(↑)	(↑)(↑)	$-0.4\ \Delta_0$	(↑↓)(↑↓)(↑↓)	00	$-\ 2.4\ \Delta_0$
7.	(↑↓)(↑↓)(↑)	(↑)(↑)	$-0.8\ \Delta_0$	(↑↓)(↑↓)(↑↓)	(↑)0	$-\ 1.8\ \Delta_0$
8.	(↑↓)(↑↓)(↑↓)	(↑)(↑)	$-1.2\ \Delta_0$	(↑↓)(↑↓)(↑↓)	(↑)(↑)	$-\ 1.2\ \Delta_0$
9.	(↑↓)(↑↓)(↑↓)	(↑↓)(↑)	$-0.6\ \Delta_0$	(↑↓)(↑↓)(↑↓)	(↑↓)(↑)	$-\ 0.6\ \Delta_0$
10.	(↑↓)(↑↓)(↑↓)	(↑↓)(↑↓)	0 0	(↑↓)(↑↓)(↑↓)	(↑↓)(↑↓)	$0\ \Delta_0$

Q7. Explain the para, dia, ferro, antiferromagnetic properties

(OR)

Explain the magnetic properties of transition meta complexes.

Ans :

Paramagnetic Substances

Substances which are weakly attracted into the magnetic field are called paramagnetic. These substances lose their magnetism on removing the magnetic field. Paramagnetism is caused by the presence of unpaired electrons and since most of the transition metal atoms have unpaired d-electrons, they are paramagnetic in behaviour.

The substances which are repelled by the magnetic field are diamagnetic when a diamagnetic substance is placed in a magnetic field, the number of lines of force passing through diamagnetic substance would be less than that which would pass through air.

Diamagnetic behaviour of the substances is due to the fact that when a diamagnetic substance is put into the magnetic field, small magnetic moments are induced into the substance. These induced magnetic moments are in opposition to the inducing field. This results in that the substance is repelled by the magnetic field.

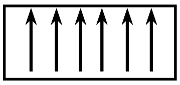
Substances having all the electrons in the paired state or having no unpaired electrons (n = 0) show diamagnetic character. When an orbital contains two electrons with opposite spins (↑↓), the magnetic moment (or magnetic field) generated by one electron is cancelled by that generated by the other electron, since magnetic moments of the two electrons are equal and opposite to each other. Thus an atom, ion or a molecule having paired electrons will be diamagnetic.

Diamagnetism is a property of completely - filled electronic subshells. Since all elements except hydrogen atom contain filled electronic shells, some diamagnetism is shown by all substances. The presence of diamagnetism in all substances is due to the interaction of the magnetic field with the paired electrons present in shells which oppose the field.

The ions of the metals of 2nd and 3rd transition series are diamagnetic, if the ions have even number of electrons.

Ferromagnetism

Substances which show permanent magnetism even in the absence of the magnetic field are called ferromagnetic substances. Such substances remain permanently magnetised, once they have been magnetised. This type of magnetism arises due to spontaneous alignment of magnetic moments due to unpaired electrons in the same direction. This is a case of large amount of paramagnetism.

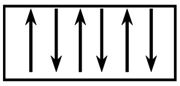


Ferromagnetism is shown by the substances which contain atoms or ions with incomplet d or f subshells. Examples of substances which show ferromagnetism are Fe, Co, Ni, Gd, Dy, number of alloys of Cu, Al and Mn, and oxides of metals of 1st transition series like CrO_2, Fe_3O_4. Ferromagnetic substances have their permeability very much greater than unity.

Anti-Ferromagnetism

Substances which are expected to posses paramagnetism or ferromagnetism on the basis of unpaired electrons but actually they possess zero net magnetic moment are called anti-ferromagnetic substances. Anti-ferromagnetism is due to the presence of equal number of magnetic moments in the opposite directions.

Many oxides of metals of 1st transitions series show anti-ferromagnetic character. Examples of such oxides are V_2O_3, CrO_3, MnO, Mn_2O_3, MnO_2, FeO, Fe_2O_3, CoO, Co_3O_4, NiO.



Magnetically concentrated systems have magnetic exchange interaction between neighbouring paramagnetic metal ion centres. The magnetic exchange interaction between the nighbouring paramagnetic ions affets the magnetic properties of the complexes and sometimes the ligand field effect. The exchange interaction occurs between the spins of the neighbouring paramagnetic ions, when the paramagnetic centres are close enough for direct or indirect orbital overlap. In fact almost all paramagnetic compounds are involved in exchange interaction to a certain extent and the interaction is dominant only at very low temperatures.

In case of anti-ferromagnetic substances these exchange interactions lead to lowering of magnetic moment compared to that expected on monomer and no-interaction basis. In anti-ferromagnetic substances the neighbouring spins are opposed to each other $(\uparrow\downarrow\uparrow\downarrow \;....)$.

Q8. Determine the magnetic sucsceptability by Gouy method.

Ans :

The Gouy Method

The apparent weight of a substance in air is greater in the presence of an applied magnetic field than in the absence of the field. The difference in weight denotes the force (F) acting on the sample to draw it into the field. This force is related to the volume susceptibility by the expression given below.

$$F = 1/2\ (k_1 - k_2)\ (H_2^2 - H_1^2)A$$

where k_1 = volume susceptibility of the sample, k_2 = volume susceptibility of air, H_2 = applied magnetic field strength, H_1 = Earth's magnetic field strength and A = cross sectional area of the sample.

The expression for F is written as

F = constant ½ $(k_1 - k_2)$, where constant = $(H_2^2 - H_1^2)\ A$

$F = \Delta w \times g$ where Δ w is the difference in the weight of the sample in the presence and absence of a magnetic field and g is the gravitational constant.

The constant, $(H_2^2 - H_1^2)A$, is evaluated by measuring F for a standard substance of known volume susceptibility. Then, by measuring F for the substance in the calibrated apparatus, k_1 is calculated. The mass susceptibility $X = k_1/\rho$ where ρ is the density of the test substance. On multiplying x by the molecular weight, the molar susceptibility χ_M is obtained.

The magnetic moment of the test substance is given by the expression

$$m = \sqrt{3RT\chi_M / N} = 2.83\sqrt{\chi_M T}$$

(i) The experiment involves the determination of two weights, one out-of-field weight and the other in-field weight, using a balance (Gouy balance). The sample is suspended from one arm of the balance into a magnetic field figure.

(ii) The sample tube (3 –10 cm) is made of pyrex glass, flat and closed at the bottom with a uniform diameter.

(iii) The test substance is uniformly packed as a powder in the tube.

(iv) $CuSO_4.5H_2O(s)$ or $Hg[Co(NCS)_4]$ can be used as a solid standard.

(v) A liquid sample is also suitable for this method in which case $NiCl_2(aq)$ is used as the standard.

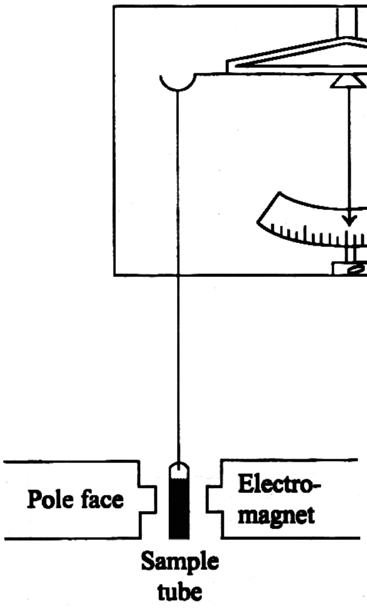


Fig.: Gouy Magnetic Balance

Q9. Describe the electronic spectra of metal complexes.

OR

What is d-d transition.

Ans : **(Imp.)**

Transitions between orbitals that mainly belong to the metal and orbitals that mainly belong to the ligand may occur in some complexes; the resulting spectra are called charge transfer spectra.

Ligand Filed Spectra

Transitions between the d orbitals of the metal (that have been split by the ligand field) produce ligand field spectra; these spectra are called d-d spectra. For example, $[Ti(H_2O)_6]^{3+}$ is pale red-purple; this colour is due to its absorption in the visible region of the electromagnetic spectrum.

The energy gap between the e_g and t_{2g} orbitals - between which d-d electronic transitions occur in a complex - depends on,

- The geometry of the complex,
- The nature of the bonded ligands and
- The oxidation state of the central metal atom.

As these three factors are of importance in characterizing a complex, the electronic spectrum of the complex can thus be used for characterizing the complex. It can furnish information on bonding and structure.

The electronic spectrum of aqueous Ti(III), a d^1 species, is shown in Figure. It has an absorption band at 20400 cm^{-1} (4900 A). It denotes the energy required to promote an electron from a t_{2g} orbital to an eg orbital. The spectroscopic term for the ground state of the gaseous Ti^{3+} ion is D; the corresponding description of the (t^1_{2g}) and (e^1_g) configurations are T_{2g} and E_g. The T_{2g} state lies 0.4 Δ_0 below, and the E_g state 0.6 Δ_0 above the values of the energies of the five d orbitals in a spherical field. The energy for the electronic transition $E_g \leftarrow T_{2g}$ increases as Δ_0 increases. The emission is denoted as $E_g \rightarrow T_{2g}$. The energy level diagram for the d^1 ion is shown in Figure.

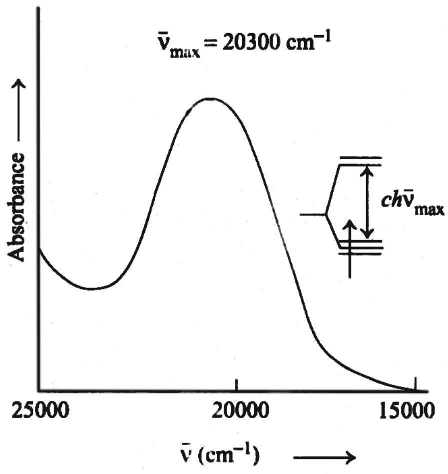


Fig.: The electronic spectrum of $[Ti(H_2O)_6]^{3+}$

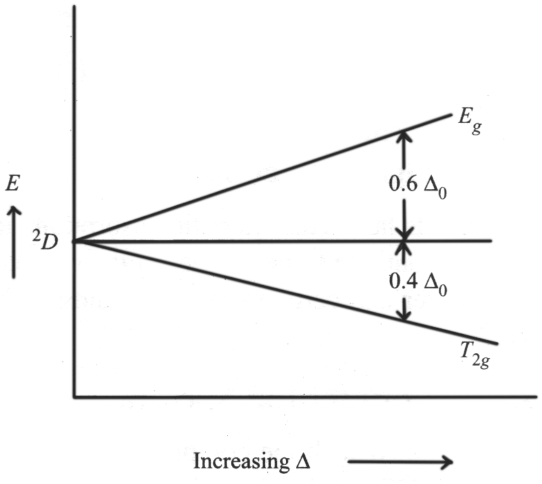


Fig.: Energy level diagram for ad^1 ion (octahedral field)

Q10. Write the detection of complex formation by various methods.

Ans :

Typical Chemical Reactions

Complex ion in a solution can be detected by the chemical reactions typical of the substances present in solution do not take place. For example, the normal solution of copper sulphate gives the tests of copper as well as sulphate ions, but whenever it is treated with excess of potassium cyanide and the resulting solution tested for copper, no positive test is obtained indicating that the copper is not present simply as copper ion but as complex ion $[Cu(CN)_4]^{3-}$ which does not dissociate into copper ions.

Solubility Measurement Method

Complex ions may be detected by the fact that whenever a sparingly soluble inorganic substance is converted into a complex, its solubility is increased. For example, silver cyanide is very sparingly soluble in water but when treated with KCN the resulting product becomes completely soluble in water indicating the formation of a complex compound and which is found to be $[Ag(CN)_2]^-$.

Conductivity Measurement (Marked Drop in Conductivity)

Strong complex may be recognized by the electrical conductivity of solution of their salts. The molar conductivity of a dilute solution depends substantially on the number of ions into which the complex dissociates. Since, complex formation decreases the number of ions, the molar conductivity will be dropped and hence, the complex can be detected. For example, the chromic chloride, $CrCl_3$, should give four ions, but actually in practice it gives only two ions, the formation of the coordination compound $[Cr(H_2O)_4Cl_2]C1$, and conductivity is proportionately decreased. Moreover, the size of the ion also alters its mobility and therefore, further decreases the conductivity of the solution.

Change in colour

The formation of complexes is commonly revealed by change in colour.

Example, anhydrous copper sulphate is colourless, while the normal hydrate $CUSO_4.5H_2O$ is blue, as is the aqueous solution. Therefore, it is assumed that in the blue salt, the copper ion contains complex-bound water.

pH Method

The addition of the ligand (HL) to a metal (M) in solution results in the release of protons as the comlexes are formed. For example, Cu^{2+} ions are treated with salicylaldoxime (Hsal) to form the complex, $[Cu(sal)_2]$ with the release of protons.

$$Cu^{2+} + 2\ Hsal \rightarrow [Cu(sal)_2] + 2H^+$$

Due to the release of H^+, the pH of the solution gets lowered. Similarly, if an aqueous solution of NH_3 is added to a soluton of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+} ions, ammine complexes of the type $[M(NH_3)_x]^{2+}$ are formed. Due to the concsumption of ammonia, concentration of free ammonia reduces. This means that the pH of the solution gets lowered. Thus change in pH of the solution can be taken as an indication for the formation of complexes.

On complexation, frequently, the magnetic susceptibility of the metal ion is altered. As complexation changes the d electron configurations, susceptibility changes therefore, magnetic susceptibility can be a diagnostic of complexation. The following magntic data illustrate this:

Species	**Fe^{3+}**	**$[Fe(CN)_6]^{3-}$**	**Co^{3+}**	**$[Co(NH_3)_6]^{3+}$**
Magnetic moment (BM)	5.9	1.7	4.9	0.0

Q11. Define Hard and Soft Acid Base.

Ans :

A hard acid is that in which electron-accepting atom is small, has high positive charge and has no electron which are easily polarised or removed. A soft acid is that in which the acceptor atom is large, carries a low positive charge or it has electrons in orbitals which are easily polarised or distored.

A Lewis base which holds its electrons strongly is called hard base, e.g., OH^-, F^- H_2O, NH_3, CH_3OCH_3 etc. On the other hand, a lewis base in which the position of electrons is easily polarised or removed is called a soft base, e.g., I^-, CO, CH_3S^-, $(CH_3)_3$ P, etc.

Q12. Classify the hard and soft acids and basis according to pearsons concept.

Ans : **(Imp.)**

Pearson's concept of hardness and softness

R.G. Pearson classified metal ions and ligands instead of class-a and class-b, into hard and soft acids and bases. Class-a are called 'hard' category and class-b are called "soft" category. Metal ions belonging to class-a belong to hard acids and ligands belong to hard bases. In a similar way metal ions of class-b belong to "soft" acids and ligands belong to "soft" bases. We know that as per Lewis, metal ions are called acids and ligands are called bases.

Hard acids & bases possess small size, small polarizability. Solft acids and bases possess large size and large polarizability.

Pearson proposed a rule to predict the stability of the compounds formed between these acids and bases. This is called Pearson's Hard Soft Acid Base rule (HSAB). This rule states that Hard acids react with hard bases, soft acids react with soft bases.

The hard or soft species belong to same class may not have same level of hardness or softness. All alkali metals belong to hard acid category but larger size, larger polarizability Cs^+ ion, compared to lower size and lower polarizability Li^+ ion is more soft. In alkali metal ions group, the hardness decreases from top to bottom. Pearson's classification of acids and bases is presented in the table.

Acids

Hard	Borderline	Soft
H^+, Li^+, Na^+, K^+, Be^{2+}	Fe^{2+}, Co^{2+}	Pd^{2+}, Pt^{2+}, Ag^+, CH_3 Hg^+,
Al^{1+}, Mg^{2+}, Ca^{2+}, st^{2+},	Ni^{2+}, Cu^{2+}	Hg^{2+}, Cu^+, Au^+, Cd^{2+}, Cs^+,
Ti^{4+}, Sc^{3+}, Cr^{3+}, Co^{3+} etc.	Zn^{2+}, Pb^{2+} etc	Pt^{4+}, Tl^+ etc.

Bases

Hard	Borderline	Soft
F^-, Cl^-, OH^-, O^{2-}, CO_3^{2-}	Br^-, NO_2^-, N_3^-,	H^-, CN^-, SCN^-, I^-
SO_4^{2-}, H_2O, ROH,	etc.	CO, R_3P, R_2S, RS^-,
R_2O, NH_3, RNH_2 etc.		SO_3^{2-}, SH^-, etc.

Table : Classification of acids & bases

Q13. Explain the applications of HSAB.

Ans :

HSAB principle is extremely useful in explaining the following:

1. Stability of complex compounds having the same ligands

The HSAB principle explains the relative stability of the following complexes:

(i) $[AgI_2]$ is stable while $[AgF_2]$ does not exist. The reason being that Ag + is a soft acid, hence, it combines with I^-. (a soft base) easily to give stable product the F^-, being hard base does not give stable product with the Ag^+, a soft acid.

(ii) $[CoF_6]^{3+}$ a species obtained by combination of hard acid (Co^{3+}) with hard base (F^-), is more stable thatn $[CoI_6]^{3-}$, a combination of hard acid & soft base.

2. Stability of complex compounds having different ligands

In a complex compound having different ligands, if all the ligands are of the same order, i.e., if all the ligands are of the same order, i.e., if all the ligands are soft or hard, the complex will be stable. For example,

(a)	$[Co(NH_3)_5\ F]^{3+}$	is more stable than	$[CoNH_3I]^{3+}$
	NH_3 and F^- are hard ligands		NH_3 is a hard ligand I^- is a soft ligand
(b)	$[Co(CN)_5\ I]^{3-}$	is more stable than	$[Co(CN)_5\ F]^{3-}$
	CN^- and I^- both are soft ligands		CN^- is a soft ligand, F^- is a hard ligand

The occurrence of some metals in nature as their ores can be explained with the help of HSAB principle. For example.

(a) Magnesium, calcium and aluminium occur in nature as $MgCO_3$, $CaCO_3$ and Al_2O_3 respectively because each of them is a combination of a hard acid (Mg^{2+}, Ca^{2+} and $A1^{3+}$) with a hard base (CO_3^{2-} and O^{2-}). Further, these metals do not exist as their sulphides becasue S^{2-} is a soft base.

The principle of hard acid + hard base; and soft acid + soft base combination has also been used to predict the course of many reactions. For example,

LiI	+	CsF	$\rightarrow$	LiF	+	CsI
(hard acid + soft base)		(soft acid + hard base)	$\rightarrow$	(hard acid + hard base)		(soft acid + soft base)
HgF_2	+	BeI_2	$\rightarrow$	BeF_2	+	HgI_2
(soft acid + hard base)		(hard acid + soft base)		(hard acid + hard base)		(soft acid + soft base)

Q14. Stability of metal complexes and overall step stability constant.

Ans :

Thermodynamic Stability

The quantitative extent of formation of metal complex is expressed in terms of the equilibrium consant of the metal complex formation reaction. This equilibrium constant is known as formation constant or stability constant designated as 'β'.

$\frac{1}{\beta}$ is instability constant.

$$m + nL \rightleftharpoons mLn$$

$$\beta = \frac{(ML_n)}{(M)[L]^n}$$

If b is large, ML_n is formed to large extent. If the stability by of ML_n is high, possibility of its formation is also high.

If b is less, stability of the complex is less and its formation also less.

Let us see the formation of ML_4 metal complexes which can be represented by the equilibrium constants of step wise formation.

$$M + L \rightleftharpoons ML \qquad k_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad k_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad k_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_3 + L \rightleftharpoons ML_4 \qquad k_4 = \frac{[ML_4]}{[ML_3][L]}$$

Q15. Determine the composition of complex by Job's method.

Ans :

Determination of the Composition of a complex (Job's Method)

Different experiment steps involved in the process are as follows :

(i) A series of solutions (say ten solutions) of a fixed volume of the complex in each case but containing different amounts of the metal ion and the ligands are prepared.

(ii) Let the total volume of the complex prepared in each of the ten solutions is 10 mL and the proportions of the metal ion and the ligand in these solutions is varied as below :

Metal ion (vol)	0	1	2	3	4	5	6	7	8	9
Ligand (vol)	10	9	8	7	6	5	4	3	2	1

Thus, it is obvious that the sum of the concentrations of the ligand (C_L) and metal ion (C_M) is constant (10) in each case and only their ratios are changed.

i.e., $C_L + C_M = C$ ... (1)

(iii) The optical density (absorbance) of each of the solutions is measured by spectrophotometer. In this process, wavelength of light is chosen which is absorbed strongly by the complex only, and not by the metal ion and the ligand.

(iv) Values of mole fraction of the ligand ($x = C_L/C$) are plotted against the optical density (absorbance) of the corresponding solution.

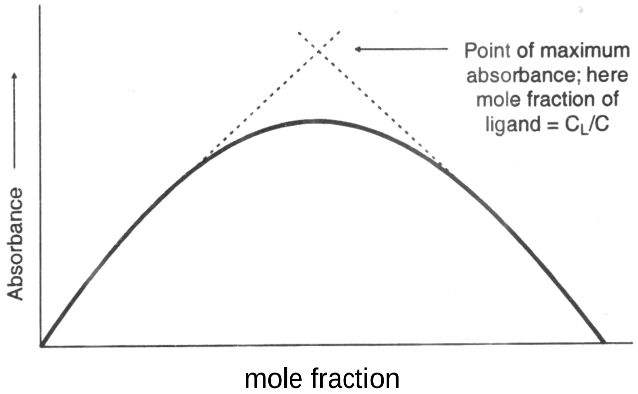


Fig.: Job's method for the determination of composition of a complex

When the logs of the curve are extrapolated, they cross each other at a point at which absorbance is maximum.

Now if the formula of the complex is ML_n, then

$$n = \frac{C_L}{C_M} \qquad \text{... (2)}$$

Dividing equation (1) throughout by C,

$$\frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C} = 1 \qquad \text{... (3)}$$

We also know that

$$x = \frac{C_L}{C} \qquad \text{... (4)}$$

From equation (3) and (4)

$$x + \frac{C_M}{C} = 1$$

$$\therefore \qquad \frac{C_M}{C} = 1 - x \qquad \text{... (5)}$$

Dividing equation (4) by (5), we get

$$\frac{C_L}{C} \times \frac{C}{C_M} = \frac{x}{1-x}$$

or

$$\frac{C_L}{C_M} = \frac{x}{1-x} \qquad \text{... (6)}$$

From equation (2) and (6),

$$n = \frac{x}{1-x} \qquad \text{... (7)}$$

Thus, by knowing the value of n from equation (7), the composition of the complex ML_n can be determined.

Limitations of Job's method

1. In case more than one species is formed in the system, the method gives unreliable results.
2. The method is applicable only when there is no change in volume on mixing the solution of the metal ion and the ligand.

Q16. Explain mole-ratio method.

(OR)

Explain the determitation of composition it a complex by mole ratio method.

Ans :

Mole-ratio Method

This method was introduced by Yoe and Jones. In this method a series of solutions are prepared containing a constant amount of the metal ions (C_m) and varying amount of the ligand (C_L) keeping the total volume constant under identical conditions. The absorbance of these solutions is measured and plotted against the ratio of moles of ligands to moles of metal ion ($R - C_L / C_m$). The break in the curve will provide the composition of the complex.

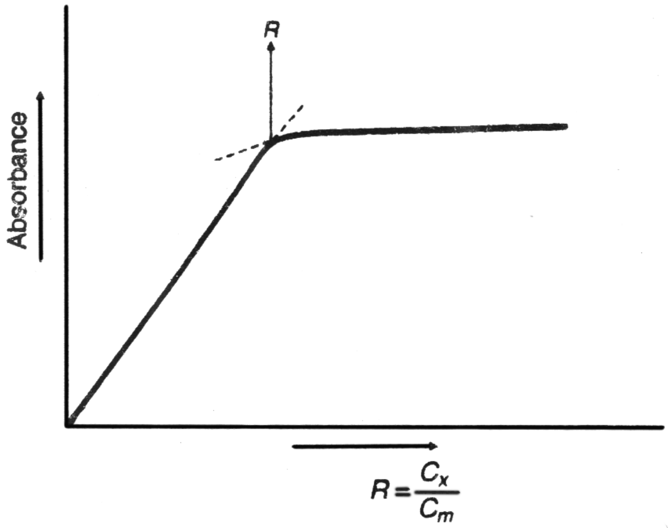


Fig.: Curve of mole-ratio method

Q17. Write any one application of coordination compound in quantitative and qualitative analysis with suitable example.

Ans :

Inorganic Qualitative Analysis

Several principles of coordination chemistry are used in inorganic qualitative analysis. The formation of metal complexes is employed in the separation and identification of some of the metals.

Separation

The principle of masking (sequestration) is used in separating some metals from each other in qualitative analysis. For example, both Cu^{2+} and Cd^{2+} form insoluble sulphides in Group II. These two metals are separated by complexing them with CN^-. Both form complexes but with a difference.

$$2CuS + 8CN^- \rightarrow 2[Cu(CN)_4]^{3-} + S_2^{2-}$$

$$CdS + 4CN^- \rightarrow [Cd(CN)_4]^{2-} + S^{2-}$$

The reaction of CN^- with CuS is an oxidation-reduction reaction coupled with complexation; Cu^{2+} is reduced to Cu^+ and then the latter is complexed to form a soluble species. This complex species has high stability and therefore it does not form the sulphide of copper with PbS. With Cd^{2+}, the reaction is only complexation and the colourless species $[Cd(CN)_4]^{2-}$ is not as stable as the copper complex and therefore it forms CdS on passing H_2S through its solution. Thus, the marked difference in the stabilities of the cyano complexes of copper and cadmium is the basis for separating these two metals.

Identification of Metals

Complex formation is used to identify several metals in qualitative analysis. The bright colours of the metal complexes render the process of identifying some metals easy and unequivalent. In some cases, the coloured complexes are insoluble in water in some other cases, they dissolve in water and produce coloured solutions. The use of complex formation (spot tests) for confirming the presence of metals in qualitative analysis.

Cu^{2+}	Ammonia solution	Deep blue solution	$[Cu(NH_3)_4]^{2+}$
Cu^{2+}	Potassium hexacyanoferrate(II)	Reddish-brown precipitate	$Cu_2[Fe(CN)_6]$
Fe^{3+}	Ammonium thiocyanate	Deep-red solution	$Fe(SCN)_3$
Fe^{3+}	Potassium hexacyanoferrate(II)	Intense-blue precipitate	$Fe_4[Fe(CN)_6]_3$

Complexometric Titrations

Certain metal ions react stoichiometrically (quantitatively) with certain ligand solutions and form stable metal complexes. For example, Ag^+ reacts quantitatively with CN^- forming a stable, soluble complex ion.

$$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$$

This reaction can be used in volumetric estimation of Ag^+ in aqueous solution [CN^- (aq) is titrated with Ag^+(aq)]. As long as there is unreacted CN^- in the solution, the contents of the reaction mixture remain clear. This is because the product is soluble. Immediately after the end point, the excess of Ag^+ added reacts with $[Ag(CN)_2]^-$ to form an insoluble product $Ag[Ag(CN)_2]$, This produces a turbidity in the reaction medium. Therefore, the appearance of turbidity signals the end point of the reaction. This titration is called a complexometric titration. A complexometric titration involves a metal ion and a ligand, which react quantitatively to form a complex species.

Q18. How the coordination complexes useful in removal of toxic metal ions in medicine.

Ans :

Complexation in Food Poisoning

Lead is a poison to the human system. It can cause encephalopathy (brain damage). This disease can produce convulsions, coma, blindness, mental retardation or even death. A person who has ingested lead is fed with $[Ca(EDTA)]^{2-}$. It reacts with the Pb^{2+} ions in the body to form $[Pb(EDTA)]^{2-}$.

$$Pb^{2+} + [Ca(EDTA)]^{2-} \rightarrow [Pb(EDTA)]^{2-} + Ca^{2+}$$

The complexed lead is excreted by the human body thus saving the victim from poisoning. The lead-EDTA complex is much more stable than the Ca-EDTA complex and therefore the Pb^{2+} ions in the body are readily trapped by EDTA. Victims who have ingested radioactive metals are treated with EDTA for detoxification. This chelant helps in quick elimination of the hazardous radioactive metals from the body.

Some of the enzymes in the human system have the cysteine unit, HOOC— CH(NH_2) — CH_2 — SH. The lead forms covalent bonds with the sulphydryl (SH) groups of cysteine and inhibits enzyme actions; this is the basis for lead poisoning. EDTA binds the lead atoms more strongly than cysteine does and consequently releases the enzyme for its normal physiological action.

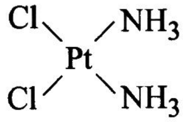
Q19. Write the use of coordination complexes in cancer therapy.

Ans : **(Imp.)**

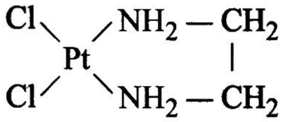
Metal Complexes in Cancer Therapy

Tumour Therapy

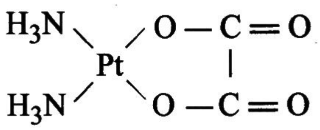
Some coordination compounds of platinum inhibit the growth of cancerous cells. Therefore, these compounds are used in cancer therapy. The structures of these antitumour complexes are represented below.



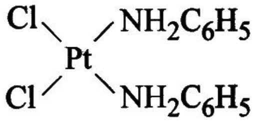
cis-Diamminedichloroplatinum(II)



cis-Dichloroethylenediamineplatinum(II)



cis-Diammineoxalatoplatinum(II)



cis-Dichlorodiphenylamineplatinum(II)

All these complexes have a common feature, namely, the cis arrangement of identical ligands. The trans isomers of these complexes do not have curative property. That chelation is involved in the mode of action of the antitumour agent with the cancer cells. The two cis groups in the drug molecule could probably get replaced by some other groups in the cancer cell, forming an association between the drug molecule and some species in the cancerous cells. Such an association may be the starting point for destroying cancerous cells. The replacement of the groups in the trans position by a chelating agent is not easy, and that is why the trans isomer of any of these complexes has no potency as a drug.

Q20. Write the use of Ziegler-Natta catalyst in polymerisation.

Ans :

Polymerisation of ethylene required high pressure, which is an expensive reaction condition. In addition, the product polythene was less crystalline and had a low melting point compared to the one formed with this catalyst. This catalyst is prepared from titanium tetrachloride ($TiCl_4$) and a trialkyl aluminimum (R_3Al), say, Et_3Al.

$$nCH_2 = CH_2 \xrightarrow[\text{ambient temperature}]{\substack{\text{Ziegler−Natta catalyst} \\ \text{1 atm pressure}}} (C_2H_4)_n$$

Q21. How complexes useful in water softening.

Ans :

Complexes in Water Softening

The wastage of soap by its reaction with Ca^{2+} and Mg^{2+} in water is prevented by sequestering these ions with complexing agents, such as polyphosphates and polydentate amino acids.

Martell and Calvin divided chelates into two categories: water-soluble chelates and water-insoluble chelates. The former are called sequestering agents which are used in aqueous solutions for masking interfering metals in a system.

$[Cu(NH_3)_4]^{2+}$ is used in some water bodies to inhibit the growth of fungi and bacteria.

S4-I-2: BIOINORGANIC CHEMISTRY

Q22. What are Essential Elements.

Ans :

Essential elements are defined as those elements which are indispensable to maintain the normal living state of a tissue or the whole body. These elements, depending upon their absolute amounts in the body, are further divided into two subgroups.

Q23. Write the biological significance of Na, Mg, Ca, Fe, Co, Ni, Cu, Zn and Chloride.

Ans :

Sodium (Na^+)

Sodium ions are more abundant outside the cells. Ex. In the blood plasma and in the intesestitial fluid surrounding the cells. They participate in transmitting nerve signals and regulate the flow of water across cell membranes.

Potassium (K)

Potassium ions present at a higher concentration inside the cells. They activate many enzymes and participate in the oxidation of glucose to produce ATP. K^+ ions involved in the transmission of nerve signals.

Calcium (Ca)

It is the major constituent of bones and teeth. It is also important in neuromuscular function internal transmission, maintanance of cell membrane integrity.

Magnesium (Mg)

Magnesium is also an essential element for animal physiology. 60% of the total magnesium present in an adult human.

Iron (Fe)

Iron very essentially utilized in the body mainly in oxygen transport & storage process in higher animals.

Cobalt (Co)

It is present in Vitamin B_{12}.

Essential for all growing tissues in humens

Deficiency of the vitamin causes anemia due to decreased production of red blood cells. –2μg of B_{12}.

Containing 0.045 – 0.09 μg cobalt is sufficient to maintain normal bone marrow function in pernicious anemia.

Nickel (Ni)

Nickel metal present in the enzyme jack bean usease. The enzyme is present in a number of plants and bacteria catalyzing hydrolysis of urea.

Nickel is one of the most cancer causing metal.

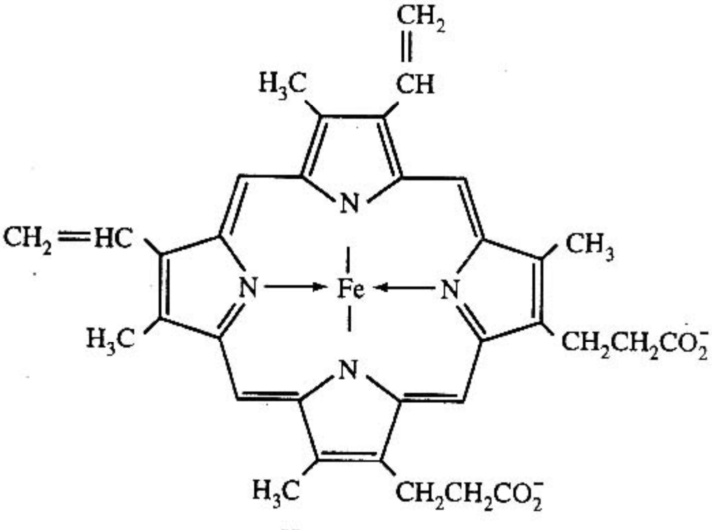
Copper (Cu)

About 60 – 100 mg of copper is present in adult human. The metal is an essential constitutent of several proteins & enzymes.

Q24. Explain the structure of Hemoglobin and the importance of Haemoglobin.

Ans : **(Imp.)**

Haemoglobin, the red pigment in red blood cells carries oxygen from the lungs to the tissues. It is called the respiratory pigment. It delivers the oxygen molecule to the myoglobin in the tissues. Haemoglobin, a protein is an iron - porphyrin complex. Figure denotes the structure of the ligand porphine. Its two H^+ ions bonded to nitrogen atoms are displaced upon coordination to iron. Complexes formed between porphine and metals are called metal porphyrins the iron - porphyrin complex is called the heme group (prosthetic group), which is a part of haemoglobin.



Heme group

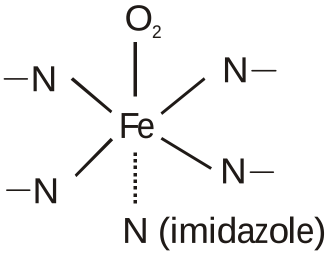
1. Each haemoglobin molecule consists of four sub-units, each unit being a folded chain. A sub - unit consists of a protein unit, (globular protein, called globin), a heme group and a histidine unit.
2. The heme unit is a chelate of iron with porphine ligand.
3. Its molecular weight is about 65,000.
4. The four polypeptide chains of haemoglobin are found in such a manner as to make the molecule spherical.

5. The iron in haemoglobin is in the Fe(II) state; it is coordinated to the four nitrogen atoms in the porphine group. Two more ligands, a histidine unit and a water molecule are also coordinated to Fe(II). The histidine ligand is the link between the heme group and the protein unit. The water molecule is denoted by a circle in the figure, because, the exact geometry of the bonding between H_2O and Fe (II) is not certain.

6. The complex is octahedral. The porphyrin ring is conjugated and planar. The charge transfer between stable and low-lying orbitals on the ring and iron is the origin for the red colour of the complex. The water ligand in haemoglobin can be readily replaced by molecular oxygen to form the red-coloured oxyhaemoglobin; this is present in the arterial blood. The water coordinated complex is called deoxyhaemoglobin; it is blue, the colour characteristic of the venous blood. As each sub-unit can bind one O_2. Each haemoglobin molecule can bind up to four O_2 molecules.

7. In oxyhaemoglobin, the Fe(II) is in the low - spin state and is diamagnetic; but in deoxyhaemoglobin, the Fe(II) is in the high -spin state and is paramagnetic. The size of Fe(II) is increased by about 30 percent, when it changes from the diamagnetic to paramagnetic state. This increase in size distorts the bonds around Fe and also the shape of the complex. In oxyhaemoglobin, the Fe and also the shape of the complex. In oxyhaemoglobin, the Fe(II) is of the right size to get into the hole at the centre of the porphyrin ring but in deoxyhaemoglobin, because of its enlargement, it is above the plane of the ring.

The O_2 molecule is bonded to the heme group as shown in Fig. 14.2



A portion of oxygenated haemoglobin

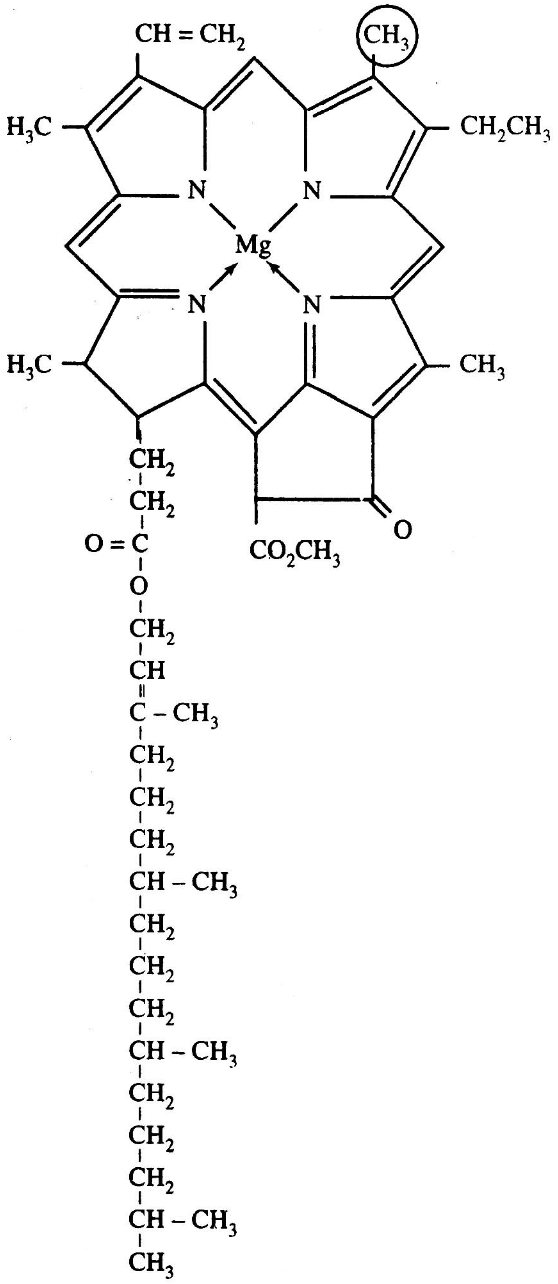
Fig. The bonding of the oxygen molecule with the heme unit of haemoglobin

The arteries carry blood to the muscles in various parts of the body, where oxygen is required. In the muscles, the oxygen is transferred to a myoglobin molecule and stored, until it is required to produce energy from glucose. When haemoglobin loses its O_2, a water molecule is again coordinated to iron. Then, the protein part of it absorbs H^+. This indirectly helps remove CO_2 from the tissues; CO_2 is converted to HCO_3^- and H^+. HCO_3^- readily dissolves in blood and H^+ is absorbed by the protein unit of haemoglobin. The impure blood returns to the heart through the veins. Then, it is pumped to the lungs where HCO_3^- is converted to CO_2 (g) and exhaled. The blood once again, picks up O_2 in the lungs and the cycle is repeated.

The oxygen-carrying process by haemoglobin is reversible; the oxyhaemoglobin complex is not too stable to render the release of O_2 at the muscles difficult. The transfer of O_2 by haemoglobin involves only Fe(II) and not Fe(III). The oxidation of Fe(II) to Fe(III), which would be irreversible and ruinous for O_2 transport, is prevented by the protein unit.

Q25. Give the structure of chlorophyll.

Ans :



Q26. Out line the fixation of CO_2 in Photosynthesis.

Ans :

Chlorophyll is a magnesium - porphyrin complex. The magnesium is at the centre of the flat heterocyclic porphyrin ring system. The metal ion is bonded to four nitrogen atoms. This complex is the green pigment in plants.

There are several kinds of chlorophyll that vary slightly in their molecular structure. In plants, chlorophyll b absorb light at wavelengths different from those absorbed by chlorophyll a, and pass the energy on to chlorophyll a, thus extending the range of light available for photosynthesis.

Chlorophyll a is a large molecule with a central atom of magnesium attached to a porphyrin ring. An hydrophobic long carbon - hydrogen chain, attached to the ring, helps anchor the molecule in the internal membranes of chloroplast. Chlorophyll b differs from chlorophyll a in having an aldehyde (CHO) group in place of the CH_3 group (indicated by a circle in the figure). Chlorophyll can convert light energy into chemical energy only when it is associated with certain proteins and embedded in a specialised membrane. Photosynthesis requires, in addition to chlorophyll, the help of four other metal complexes, a manganese complex, two iron complexes (cytochromes and ferredoxins) and a copper complex (plastocyanin).

Chlorophyll b differs from chlorophyll a in having an aldehyde (CHO) group in place of the CH_3 group.

(i) Chlorophyll absorbs light in the red region (near 700 nm) from the sunlight and supplies the absorbed energy for photosynthesis; in this synthesis, CO_2 is converted into sugars.

$$x\,CO_2 + y\,H_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} \underset{\text{carbohydrate}}{C_x(H_2O)_y} + x\,O_2$$

CO_2 is "fixed" and oxygen is a by -product in this process. Photosynthesis occurs not only in higher plants but also in algae and certain bacteria. It involves the conversion of light energy into chemical energy.

(ii) Many individual enzyme-catalysed reactions occur in photosynthesis. The process begins with the absorption of light by chlorophyll. The green colour of chlorophyll and therefore, its capacity to absorb sunlight in the visible region, is primarily due to its extended conjugated system. Chlorophyll traps photons of sunlight and supplies these to the plant cells to reduce carbon dioxide to carbohydrates and to oxidise water to oxygen.

(iii) Magnesium in it makes the molecule rigid so that the energy absorbed is not lost thermally through molecular vibrations. In addition, it enhances the rate at which the short-lived excited state initially formed by photon absorption is transformed into the corresponding triplet state; the triplet state has a longer lifetime and therefore can transfer its excitation energy into the redox chain.

Short Question and Answers

1. What are Low Spin - High Spin Complexes?

Ans :

Low Spin Complex

In presence of strong field ligands, d-orbitals are splitted to greater extent hence t_{2g} orbitals are paired first then the $e^{\ominus}$ enter into eg orbitals. That is pairing is taking against Hunds rules and the complex formed is known as low spin complex as magnetic moment of formed complex is less than the metal ion.

Example

$[Mn\,(CN)_6]^{-4}$

Oxidation state of Mn = +2

Electronic configuration of Mn^{+2} = d^5s^0

High Spin Complex

In the presence of weak field ligands pairing does not occur against the Hund's rule due to less energy difference between d-orbitals. If spin magnetic moment of complex remains some or they increased in the presence of ligand field then the resulting complex is known as high spin complex.

Ex: $\left[Ni(NH_3)_6\right]^{+2}$

Oxidation state for Ni = +2

Electronic configuration of Ni^{+2} = $d^8\,s^0$

NH_3 is weak field ligand

---

2. What is Crystal Field Stabilization Energy?

Ans :

Crystal Field Stabilization Energy

Under the influence of crystal field, the d-orbitals of the metal split into two energy levels (higher and lower energy levels) Therefore electrons enter selectively into lower energy d-orbitals. Thus the energy of the complex being formed is lowered, the complex attains stability. The energy is called crystal field stabilization energy (CFSE).

In $\left[Ti(H_2O)_6\right]^{+3}$ complex single $e^{\ominus}$ is present Ti^{+3}. In free metal ion all the 5d - orbitals are degenerate. Therefore this can enter any of these 5 d-orbitals.

3. Write the formula for the Calculation of CFSE.

Ans :

Octahedral complex = $[-0.4 + t_{2g}\ e^{\Theta}s + 0.6 \times eg\ e^{\Theta}]\Delta_0$

Tetrahedral complex = $[-\ 0.6 \times eg\ e^{\Theta}s + 0.4 \times t_{2g}e^{\Theta}]\Delta t$

The electronic arrangement, CFCE values of octahedral.

---

4. What are the para, dia and ferromagnetic substances?

Ans :

Paramagnetic Substances

Substances which are weakly attracted into the magnetic field are called paramagnetic substances.

Diamagnetic Substances

Substances which are repelled to magnetic field are called diamagnetic substances.

Ferromagnetism

Substances which show permanent magnetism even in the absence of the magnetic field are called ferromagnetic substances.

---

5. Write the detection of complex formation by Solubility Measurement Method.

Ans :

Solubility Measurement Method

Complex ions may be detected by the fact that whenever a sparingly soluble inorganic substance is converted into a complex, its solubility is increased. For example, silver cyanide is very sparingly soluble in water but when treated with KCN the resulting product becomes completely soluble in water indicating the formation of a complex compound and which is found to be $[Ag(CN)_2\ ]^-$.

---

6. Write the detection of complex formation by Conductivity Measurement (Marked Drop in Conductivity)

Ans :

Conductivity Measurement (Marked Drop in Conductivity)

Strong complex may be recognized by the electrical conductivity of solution of their salts. The molar conductivity of a dilute solution depends substantially on the number of ions into which the complex dissociates. Since, complex formation decreases the number of ions, the molar conductivity will be dropped and hence, the complex can be detected. For example, the chromic chloride, $CrCl_3$, should give four ions, but actually in practice it gives only two ions, the formation of the coordination compound $[Cr(H_2O)_4Cl_2\ ]C1$, and conductivity is proportionately decreased. Moreover, the size of the ion also alters its mobility and therefore, further decreases the conductivity of the solution.

---

7. Write the use of Ziegler-Natta catalyst in polymerisation.

Ans :

Polymerisation of ethylene required high pressure, which is an expensive reaction condition. In addition, the product polythene was less crystalline and had a low melting point compared to the one formed with this catalyst. This catalyst is prepared from titanium tetrachloride ($TiCl_4$) and a trialkyl aluminimum (R_3Al), say, Et_3Al.

$$nCH_2 = CH_2 \xrightarrow[\text{ambient temperature}]{\text{Ziegler–Natta catalyst, 1 atm pressure}} (C_2H_4)_n$$

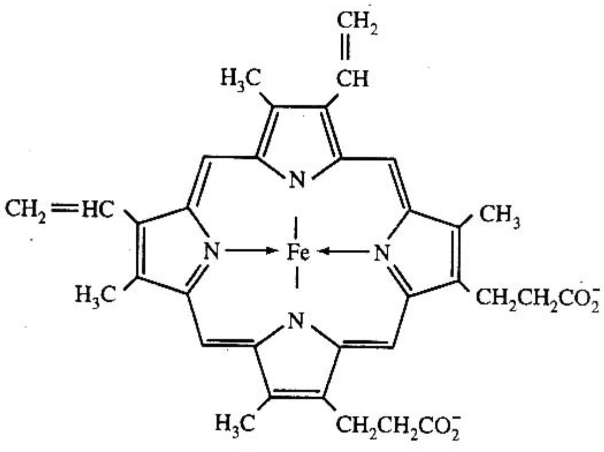
8. What are Essential Elements?

Ans :

Essential elements are defined as those elements which are indispensable to maintain the normal living state of a tissue or the whole body. These elements, depending upon their absolute amounts in the body, are further divided into two subgroups.

9. Draw the structure of Hemoglobin.

Ans :



Heme group

10. Write the biological significance of Na, Mg and Ca.

Ans :

Sodium (Na^+)

Sodium ions are more abundant outside the cells. Ex. In the blood plasma and in the intesestitial fluid surrounding the cells. They participate in transmitting nerve signals and regulate the flow of water across cell membranes.

Potassium (K)

Potassium ions present at a higher concentration inside the cells. They activate many enzymes and participate in the oxidation of glucose to produce ATP. K^+ ions involved in the transmission of nerve signals.

Calcium (Ca)

It is the major constituent of bones and teeth. It is also important in neuromuscular function internal transmission, maintanance of cell membrane integrity.

Choose the Correct Answers

1. Fe^{3+} forms a high-spin octahedral complex; then its magnetic moment is [a]

(a) 5.92 BM (b) 0 BM

(c) 1.73 BM (d) None of the above

2. The magnitude of Δ_0 value will depend upon, [d]

(a) Charge of the central metal ion

(b) Nature of the ligand

(c) Principal quantum number of the d-electron

(d) All the above

3. The complex ion developing the highest crystal field splitting energy is [c]

(a) $[Co(NH_3)_6]^{2+}$ (b) $[Rh(NH_3)_6]^{3+}$

(c) $[Ir(NH_3)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

4. The order of increasing energies of different d-orbitals in a square-planar geometry is [d]

(a) $d_{xy} = d_{xz} = d_{yz} < d_{x^2-y^2} = d_z^2$ (b) $d_{x^2-y^2} = d_z^2 = d_{xy} = d_{xz} = d_{yz}$

(c) $d_{xz} = d_{yz} = d_{xy} < d_z^2 < d_{x^2-y^2}$ (d) $d_{xz} = d_{yz} = d_z^2 < d_{xy} < d_{x^2-y^2}$

5. CFSE for a high-spin system is zero. Its electronic distribution is [d]

(a) $(t_{2g})^4 (e_g)^0$ (b) $(t_{2g})^6 (e_g)^3$

(c) $(t_{2g})^4 (e_g)^2$ (d) $(t_{2g})^3 (e_g)^2$

6. The one with the largest Δ_0 value is [c]

(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Fe(NH_3)_6]^{3+}$

(c) $[Ru(CN)_6]^{3-}$ (d) $[Ru(H_2O)_6]^{2+}$

7. The CFSE for a high-spin octahedral complex of a d^6 ion is [d]

(a) $-0.6\ \Delta_0$ (b) $1.2\ \Delta_0$

(c) $1.8\ \Delta_0$ (d) $-0.4\ \Delta_0$

8. Crystal field splitting energy (Δ_{sp}) in square planer complexes. [a]

(a) $1.3\ \Delta_0$ (b) $0.45\ \Delta_0$

(b) $.95\ \Delta_0$ (d) $0\ \Delta_0$

9. The complex formation is identified qualitatively by [d]

(a) Colour change (b) P^H change

(c) Counductivity change (d) All the above

10. The process of chelation effects the stability of complex [a]

(a) Increases (b) Decreases

(c) Remain change (d) None of the above

11. The metal present in vitamin B_{12} is : [c]

(a) Iron (b) Magnesium

(c) Cobalt (d) Copper

12. The iron present in haemoglobin is in : [a]

(a) Ferrous state (b) Ferric state

(c) Metallic state (d) None of the above

13. Anaemia is caused by deficiency of : [a]

(a) Fe (II) (b) Fe (III)

(c) Zn (d) Mg

14. Which of the following elements in poisonous to living systems even in small doses ? [d]

(a) P (b) Na

(c) Zn (d) Hg

15. The element needed by the body in small amounts but acts as a poison in large amount is : [c]

(a) Pb (b) Hg

(c) Cu (d) None of the above

16. The element which has toxic effect in very small does but is poisonous in large does is : [b]

(a) Pb (b) As

(c) Hg (d) None of the above

17. The element present in chlorophyll, green colouring matter of plants, is : [a]

(a) Mg (b) Zn

(c) Fe (d) Cu

18. The element present in every body cell, bones and teeth is : [d]

(a)	Ca	(b)	Fe
(c)	Na	(d)	P

19. Dimercaprol forms ring with : [d]

(a)	As	(b)	Pb
(c)	Hg	(d)	As and Hg

20. Haemoglobin forms quite stable compound with : [b]

(a)	O_2	(b)	CO
(c)	None	(d)	Both

Fill in the blanks

1. The apparatus which used to calculate the magnetic movements is ________.
2. Transition between d-orbitals of the metal are known as ________.
3. Ziegler - Natta catalyst is ________ and ________.
4. The complex used in cancer therapy is ________.
5. Anli ferromagnetic substances examples ________.
6. Ferromagnetic substances examples are ________.
7. Crystal field stabilization energy formula in octahedral complexes is ________.
8. Lead poisioning is treated by ________.
9. The catalyst used in polymerisation of ethenlene is ________.
10. The mole fraction of the complex is n = ________
11. In haemoglobin, iron is present in _______ form.
12. Excess of Na^+ ions in blood _______ blood pressure.
13. Deficiency of iron in diet causes _______.
14. A common antidote for mercury poisoning is the _______.
15. Excess addition of sodium to diet causes an excessive elimination of _______ from the body.
16. S_N^1 follows _______.
17. S_N^2 follows _______.
18. HSAB principle is _______.
19. Mg, Ca, occur in nature as _______.
20. Hard Acid + Hard base forms _______.

ANSWERS

1. Gouymagnetic balance
2. d-d tranitations
3. Titanium tetra chloride & TriAlkylaluminium
4. Diamine dichloro platinum

5. V_2O_3, CrO_3, MNO
6. CrO_2, Fe_3O_4
7. $0.4 + t_2ge^- + 0.6\ x + ege^-)\Delta^0$
8. $(Ca\ EDTA)^2$
9. Zigler - Natta Catalyst
10. $n = \frac{x}{1-x}$
11. Fe^{2+}
12. Increases
13. Anaemia
14. Raw egg
15. Potassium ions
16. Dissociative mechanism & first order kinetics
17. Associative mechanism
18. Hard & soft acids bases
19. Carbonates & oxides
20. Stable complex

One Mark Answers

1. What is crystal field splitting ?

Ans :

The splitting of five degenerate d-orbitals into different group of orbitals of different energies under the influence of crystal field is known as crystal field splitting. It is one of the important aspect of crystal field theory. It takes place in common structures such as octahedral, tetrahedral and square planar.

2. What is a low spin complex?

Ans :

A complex having less number of unpaired electrons is called as low spin complex.

3. Give two examples for high spin complexes.

Ans :

(CoF_6), $[Cr(NH_3)_6]^{+3}$

4. List the stability types for metal complexes.

Ans :

The stability types for metal complexes are,

(i) Kinetic stability

(ii) Thermodynamic stability.

5. Find μ_s when n = 1.

Ans :

$$\mu_s = \sqrt{n(n+2)}$$

$$\Rightarrow \mu_s = \sqrt{1(1+2)}$$

$$\therefore \mu_s = \sqrt{3} = 1.732 \text{ B.M.}$$

6. List the factors affecting stability of metal complexes.

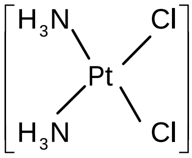
Ans :

1. Environmental factors. (Temperature and pressure).
2. Effects of central ion (Ionic charge and Ionic size).
3. Effects of the ligands (Size and charge of Ligand, steric effect, chelation effect).

7. What is Cisplatin?

Ans :

Cisplatin is an anticancer drug. It cures both A and B stage carcinomas (a death causing testicular cancer).



8. Give two examples for Zieglar-Natta catalyst.

Ans :

(i) Triethyl Aluminium $(C_2H_3)_3$A1.

(ii) Titanium tetrachloride, $TiCl_4$.

9. How many ATP are used in dark reaction?

Ans :

The Calvin cycle uses 18 ATP and 12 NADPH molecules to produce one glucose molecule.

10. Name two pigments which absorb sunlight other than chlorophyll.

Ans :

Fucoxanthin and carotenoids.

UNIT - II

(Organic Chemistry)

S4-O-1: Carbohydrates

Introduction: Classification and nomenclature. Monosaccharides: All discussion to be confined to (+) glucose as an example of aldo hexoses and (-) fructose as example of ketohexoses. Chemical properties and structural elucidation: Evidences for straight chain pentahydroxy aldehyde structure. Number of optically active, isomers possible for the structure, configuration 15 of glucose based on D-glyceraldehyde as primary standard (No proof for configuration is required). Evidence for cyclic structure of glucose (Pyranose structure, anomeric carbon and anomers). Proof for the ring size (methylation, hydrolysis and oxidation reactions). (Haworth formula and chair conformational formula). Structure of fructose: Evidence of 2 – ketohexose structure. Same osazone formation from glucose and fructose, Hydrogen bonding in osazones, cyclic structure for fructose (Furanose structure, Haworth formula).

Inter Conversion of Monosaccharides: Arabinose to D-glucose, D- mannose (kiliani – Fischer method). Epimers, Epimerisation- Lobry de bruyn van Ekenstein rearrangement. D-glucose to D-arabinose by Ruff's degradation. Aldohexose(+) (glucose) to ketohexose (–) (fructose) and Ketohexose(Fructose) to aldohexose (Glucose).

S4-O-2: Amino acids and proteins

Classification. Methods of synthesis: General methods of synthesis of alpha amino acids (specific examples – Glycine, Alanine, Valine and Leucine) by following methods: a) From halogenated Carboxylic acid b)Malonic ester synthesis c) strecker's synthesis. Physical properties: Optical activity of naturally occurring amino acids. Zwitter ion structure – salt like character, definition of isoelectric point. Chemical properties: General reactions due to amino and carboxyl groups – Lactams from gamma and delta amino acids by heating peptide bond (amide linkage). Structure and nomenclature of peptides. Primary structure of proteins, dipeptide synthesis

S4-O-3: Heterocyclic Compounds

Introduction and definition: 5 membered ring compounds with one hetero atom Ex. Furan. Thiophene and pyrrole. Importance of ring systems – Numbering. Aromatic character Resonance structures: Explanation of feebly acidic character of pyrrole, electrophillic substitution, Halogenation, Nitration and Sulphonation. Reactivity of furan as 1, 3 -diene, Diels Alder reactions (one example). Sulphonation of thiophene purification of Benzene obtained from coal tar). Preparation of furan, Pyrrole and thiophene Paul - Knorr synthesis. Structure of pyridine, Basicity – Aromaticity – Comparison with pyrrole– preparation by Hantsch method and properties – Reactivity towards Nucleophilic substitution reaction – chichibabin reaction.

S4-O-1: CARBOHYDRATES

Q1. Write the classification of carbohydrates with examples.

Ans :

Carbohydrates

Carbohydrates are defined as compounds containing carbon, hydrogen, oxygen. The two elements being present in the same ratio as in water. They are regarded as the hydrates of carbon. The formula $C_x(H_2O)_y$.

$C_6 H_{12}O_6$	$C_{12} H_{22} O_{11}$	$(C_6 H_{10} O_5)_n$
Glucose/Fructose	Sucrose	Starch

Carbohydrates are defined as the optically active polyhydroxy aldehydes or ketones which yield these on hydrolysis.

$$xCO_2 + xH_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} \underset{\text{Carbohydrate}}{(CH_2O)_x + O_2}$$

Carbohydrates may be classified into two broad groups. Sugars and non-sugars (polysaccharides).

1. **Sugars**

Sugars are sweet, crystalline substances and soluble in water. They are sub divided into two groups monosaccharides the monosaccharides are polyhydroxy - aldehydes or ketones which cannot be hydrolysed further to simpler sugars. They many again be classified according to the type of carbonyl group and the number of carbon atoms in the molecule.

Aldoses - having aldehydic group

Ketoses - having ketonic group.

2. **Oligosaccharides**

These yield two to ten monosaccharide molecules on hydrolysis. They again classified into various groups depending upon the number of monosaccharide units formed on hydrolysis.

Disaccharides these are sugars which on hydrolysis give two moles of the same or different monosaccharides. Sucrose yields one mole each of glucose & fructose.

$$C_{12} H_{22} O_{11} + H_2O \rightarrow C_6 H_{12} O_6 + C_6 H_{12} O_6$$

$$C_{12} H_{22} O_{11} + H_2O \rightarrow 2C_6 H_{12} O_6$$

3. **Trisaccharides**

These give three moles of monosaccharides on hydrolysis. E.g., Raffinose $C_{18}H_{32}O_{16}$.

4. **Tetrasaccharides**

These give four moles of monosaccharides on hydrolysis. E.g., Stachyose. $C_{24} H_{42} O_{21}$.

All monosaccharides and all disaccharides (Except Sucrose) reduce fehling solution and tollens reagent $\therefore$ termed as reducing sugars which donot reduce fehling solution and tollen's reagent are termed as non-reducing sugars.

Non-Sugars or Polysaccharides

They are usually tasteless, amorphous solids and are either insoluble in water or form colloidal suspension. Chemically polysaccharides are polymers of monosaccharides. Ex: Cellulose, Inulin.

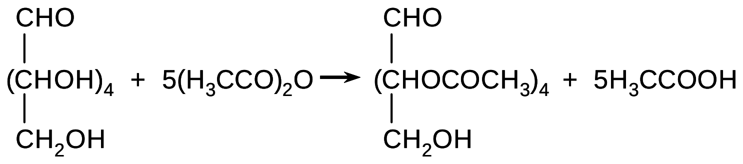
Q2. Give the evidences for straight chain of pentahydroxy aldehyde structure of Glucose.

Ans : **(Imp.)**

Evidence for Straight Chain Pentahydroxy Aldose

1. Alcohol Group Reaction Acetylation

Glucose reacts with acetic anhydride in the presence of anhydrous zinc cholride to form penta-acetyl glucose.



$$\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array} + 5(H_3CCO)_2O \longrightarrow \begin{array}{l}CHO\\ |\\ (CHOCOCH_3)_4\\ |\\ CH_2OH\end{array} + 5H_3CCOOH$$

Pentaacetyl glucose

2. Formation of Glucosate

Glucose reacts with metallic hydroxides like $Ca(OH)_2$.

$Sr(OH)_2$, $Cu(OH)_2$ to form water soluble glucosates.

$$C_6H_{11}O_5 . OH + HO . Ca . OH \rightarrow C_6H_{11}O_5 O . Ca . OH + H_2O$$

Calcium glucosate(water soluble)

3. **Oxidation:** Keto group reactions.

Tollen's Test: Glucose reduces tollens reagent on heating to form a silver mirror.

$$HOH_2C - (CHOH)_4CHO + \underset{\text{Tollen's reagent}}{Ag_2O} \longrightarrow \underset{\text{Gluconicacid}}{HOH_2C - (CHOH)_4 - COOH} + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

$$AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3 \qquad 2AgOH \longrightarrow Ag_2O + H_2O$$

Fehling's Test: Glucose reduces fehling solution on heating to form a red precipitate of cuprous oxide.

$$HOH_2C - (CHOH)_4CHO + \underset{\text{Fehling}}{2CuO} \longrightarrow \underset{\text{Gluconicacid}}{HOH_2C - (CHOH)_4 - COOH} + \underset{\text{Red ppt:}}{Cu_2O\downarrow}$$

$$.CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4 \quad 2Cu(OH)_2 \longrightarrow 2CuO + 2H_2O$$

Bromine Water

Mild oxidizing agents like bromine water oxidises glucose to gluconic acid.

$$\text{HOCH}_2\,.\,\text{CH(OH)}_4\,.\,\text{CHO} + \text{(O)} \xrightarrow{\text{Br}_2 + \text{H}_2\text{O}} \text{HOH}_2\text{C}\,.\,\text{(CHOH)}_4\,.\,\text{COOH}$$

Other ractions Gluconic acid

Reaction with Alkali's

Glucose warmed with strong sodium hydroxide solution glucose first turns yellow, then brown and finally gives a resinous mass.

Q3. Write the number of optically active isomers possible for the structure of glucose.

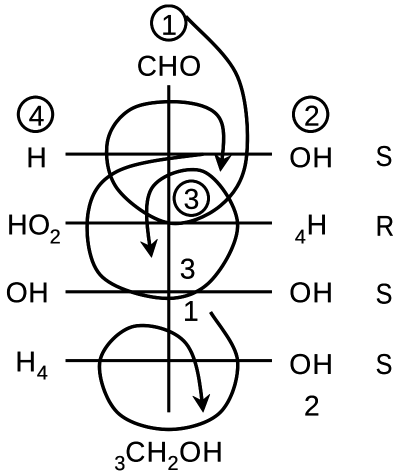
Ans :

Configuration of Glucose

Glucose possesses four asymmetric carbon atoms it can exist in $2^4 = 16$ optically active forms i.e., eight pairs of enantiomers. D and L of glucose, mannose, galactose, allose, altrose, gulose, idose, and talose.

Q4. Describe the configuration of glucose.

Ans :



C_2 – S configuration

C_3 – R configuration

C_4 – S configuration

C_5 – S configuration

Q5. Write the evidences for the cyclic structure of glucose.

Ans :

Evidence for Straight Chain of Six Carbons

1. Reduction of glucose with concentrated HI and phosphorus gives 2 – Idohexane and n-Hexane. This indicates that six carbon atoms in glucose are present in a straight chain.

$$H_2COH\ .\ (CHOH)_4\ .\ CHO \xrightarrow[\text{Red P}]{\text{Conc . HI}} H_3C - (CH_2)_3 - CHI\ .\ CH_3$$

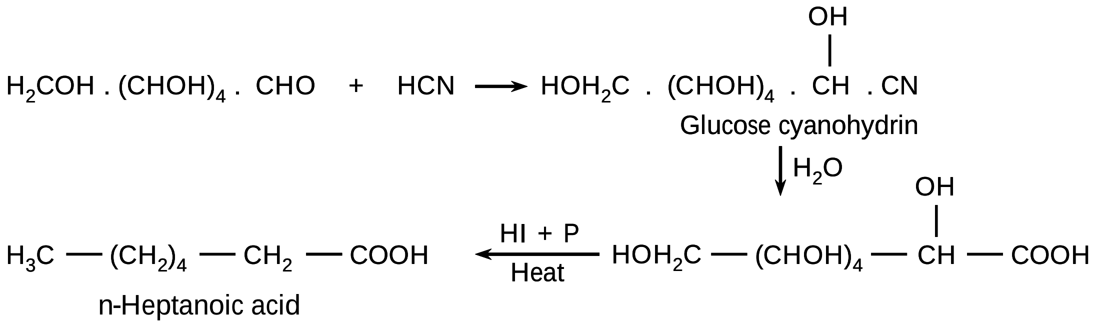
2 – Iodohexane

$$H_2COH\ .\ (CHOH)_4\ .\ CHO \xrightarrow[\text{Heating with HI + P}]{\text{Prolonged}} H_3C\ .\ (CH_2)_3\ .\ CH_3$$

n – Hexane

2. Glucose when oxidised with bromine water gives gluconic acid which when reduced with excess of HI gives n-hexanoicacid $H_3C - (CH_2)_4 - COOH$ confirming the presence of a straight chain of six carbon atoms in glucose.

3. Glucose cyanohydrin on hydrolyse followed by reduction with HI gives n – Heptanoic acid further confirming the presence of a straight carbon chain in glucose.



$$H_2COH\ .\ (CHOH)_4\ .\ CHO + HCN \longrightarrow HOH_2C\ .\ (CHOH)_4\ .\ \overset{\overset{\displaystyle OH}{|}}{CH}\ .\ CN$$

Glucose cyanohydrin

$$\downarrow H_2O$$

$$H_3C - (CH_2)_4 - CH_2 - COOH \xleftarrow[\text{Heat}]{\text{HI + P}} HOH_2C - (CHOH)_4 - \overset{\overset{\displaystyle OH}{|}}{CH} - COOH$$

n-Heptanoic acid

Formation of n-heptanoic acid indicates that in glucose all the six carbon atoms are present in a straight chain.

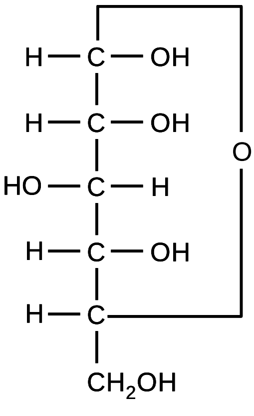
Q6. Define anomers and mention the anomeric carbon atoms present in glucose.

Ans : **(Imp.)**

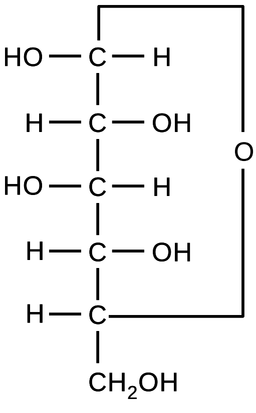
Formulation of Two Anomeric Glucosides

In the ring structure one new asymmetric centre have two different arrangements to give two isomeric glucoses.

In carbohydrate chemistry the two isomers differing only in the configuration of C_1 (in aldoses) or C_2 (in ketoses) are known as anomers.

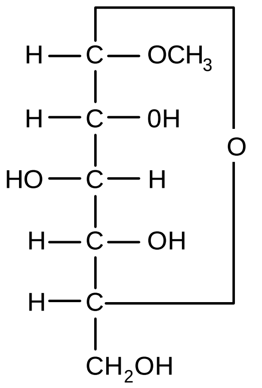


α — D — Glucose

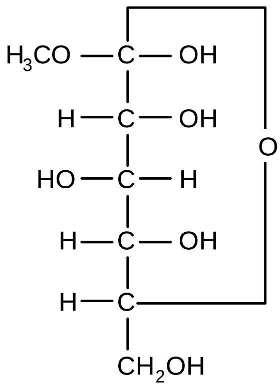


β — D — Glucose

The existence of two methyl glucosides



α — Methyl glucoside



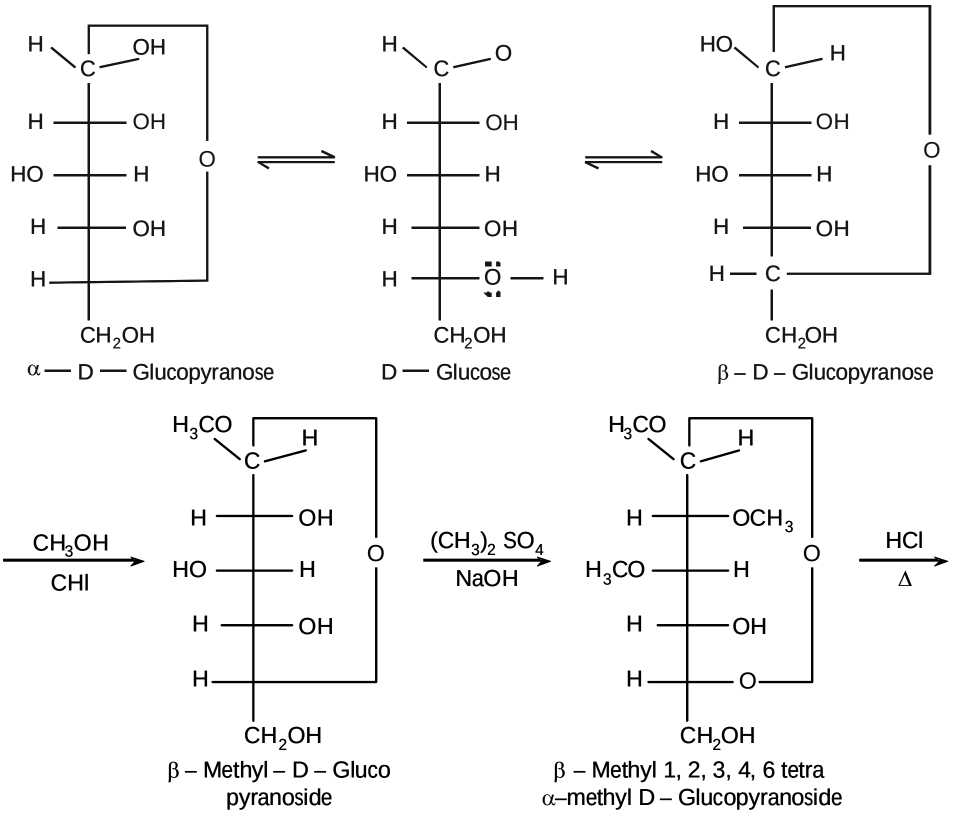
β — Methyl glucoside

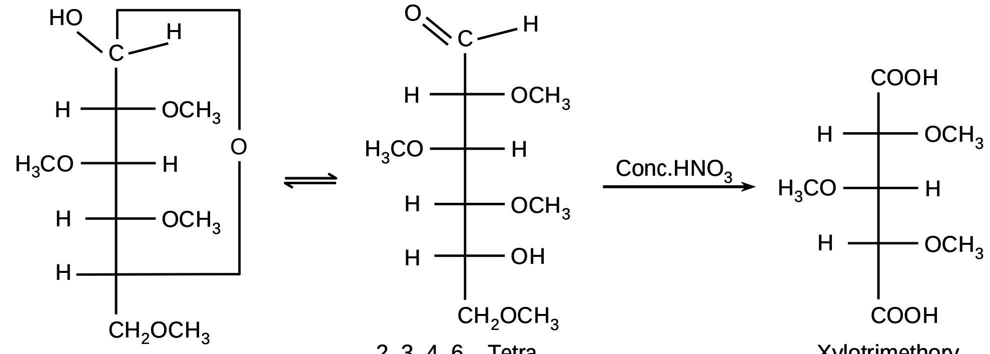
Q7. Describe the proof for the ring size in glucose.

Ans : **(Imp.)**

Proof for the Ring Size in Ring Structure

The glucose is treated with a mixture of one mole alcohol and one mole HCl to form a mixture of a β – Methyl glucosides. This mixture is separated and one glucoside is obtained. This is treated with dimethyl Sulphate $(CH_3)_2SO_4$ in presence of NaOH. Methyl - Tetra - O - Methyl glucoside is formed. This glucoside on treatment with HCl. The α – CH_3 present on acetyl carbon is converted into – OH. Tetra – O – methyl glucose is oxidised with concentrate HNO_3 to form xylotrimethoxy glutaric acid. This is a meso compound. The glucose gave finally six membered glutaric acid. This confirmed the pyranose ring structure.





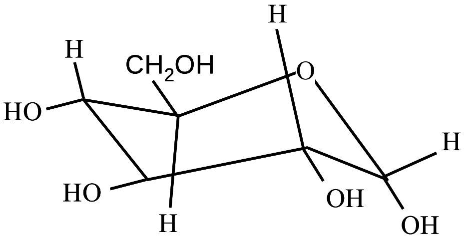
2, 3, 4, 6 – Tetra – O – methyl D – Gluco –pyranose

2, 3, 4, 6 – Tetra – O – methyl – D – Glucose

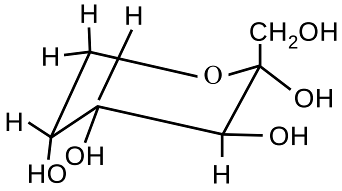
Xylotrimethory Glutaric acid

Q8. Write the confirmation structures for Glucose and Fructos.

Ans :



α – D(+) – Glucopynanose



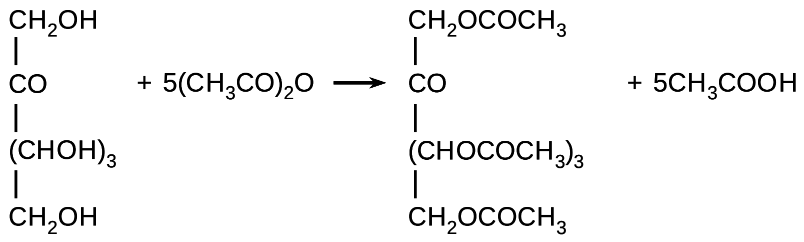
α – D(–) – Fructopyranose

Q9. Write any two evidences for the presence of 2-ketohexose in Fructose structure.

Ans :

Reactions of the alcoholic grops

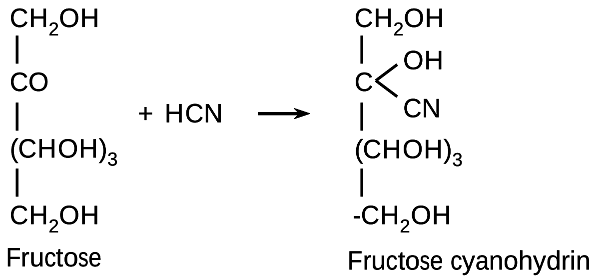
(i) Acetylation : Like glucose, fructose reacts with acetic anhydride or acetyl chloride to form penta-acetyl fructose.



$$\begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + 5(CH_3CO)_2O \longrightarrow \begin{array}{l} CH_2OCOCH_3 \\ | \\ CO \\ | \\ (CHOCOCH_3)_3 \\ | \\ CH_2OCOCH_3 \end{array} + 5CH_3COOH$$

Fructose Penta-acetyl fructose

(ii) Action of hydrogen cyanide : Fructose forms cyanohydrin.



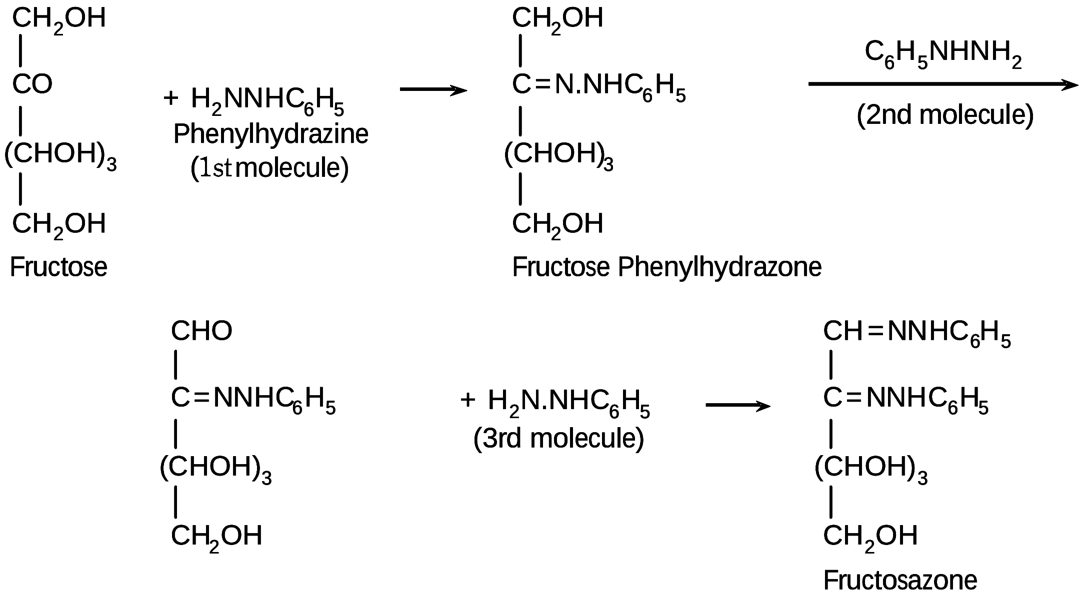
$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + HCN \longrightarrow \begin{array}{l} CH_2OH \\ | \\ C{<}^{OH}_{CN} \\ | \\ (CHOH)_3 \\ | \\ \text{-}CH_2OH \end{array}$$

Q10. Write the reaction of osazone in Fructose.

Ans :

Action of Phenylhydrazine

Fructose reacts with phenylhydrazine to form fructose phynylhydrazone. The latter reacts with excess of phenylhydrazine to form fructosazone exactly in the same way as glucose.



$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2NNHC_6H_5 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ C{=}N.NHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} \xrightarrow[\text{(2nd molecule)}]{C_6H_5NHNH_2}$$

$$\begin{array}{l} CHO \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array} + H_2N.NHC_6H_5 \longrightarrow \begin{array}{l} CH{=}NNHC_6H_5 \\ | \\ C{=}NNHC_6H_5 \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

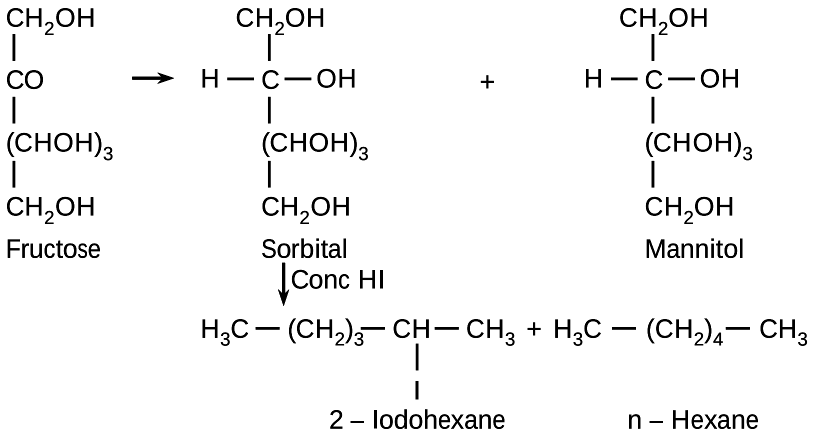
It is important to note that glucosazone and fructosazone have the same structure and m.p. (250°C); actually the osazones obtained from glucose and fructose are one and the same. Now since, we know that osazone formation involves only C_2 and C_1 of the compound, it is beyond doubt that C_3, C_4, C_5 and C_6 of glucose and fructose are exactly identical. In other words, the two sugars differ only in the first two carbon atoms.

Q11. Write the evidences for 2-ketohexose structure present in fructose.

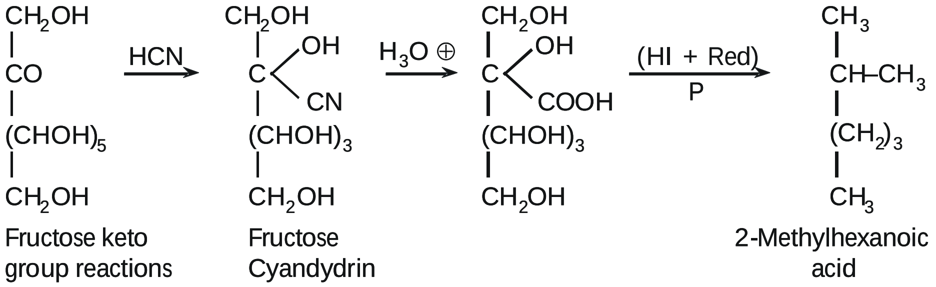
Ans :

Evidence for Straight Chain 2 - Ketohexose

Fructose on reduction gives a mixture of sorbitol and mannitol which on reduction with Conc. HI and red phosphorous gives a mixture of 2-Iodohexane and n-hexane, This indicates that the six carbon atoms in fructose are arranged in a staright chain.



Straight chain of six carbon atoms is further proved by fructorse cyanohydrin on hydrolysis followed by reduction with HI and redphosphorous give 2 - methylhexanoicacid.



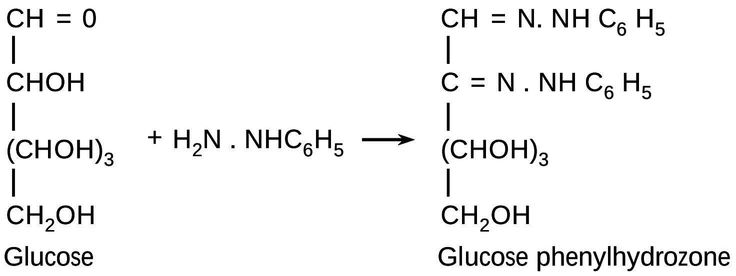
Q12. Write the osazone formation for glucose and fructose and explain the possibility of hydrogen bonding in glucose.

Ans :

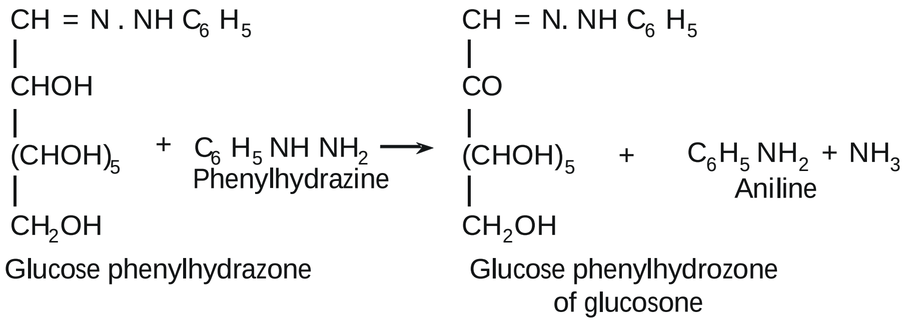
Osazone Formation

Glucose reacts with phenylhydrazine in equimolecular proportion to form phenylhydrazone. The normal aldehydes glucose reacts with excess of phenylhydrazine to form glucosozone.

1. One molecule of phenylhydrazine reacts with the aldehydic group of glucose to form glucose phenylhydrozone.

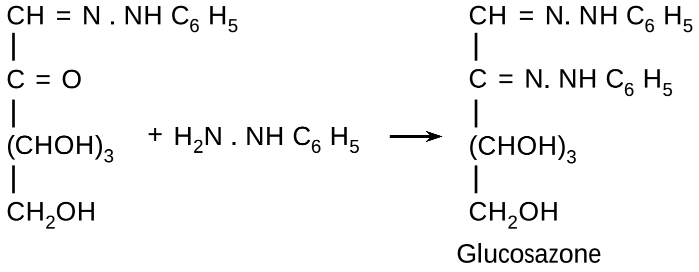


2. The second molecule of phenylhydrazine oxidises the secondary alcoholic group adjacent to the aldehydic group to a ketonic group and itself is reduced to aniline and ammonia.

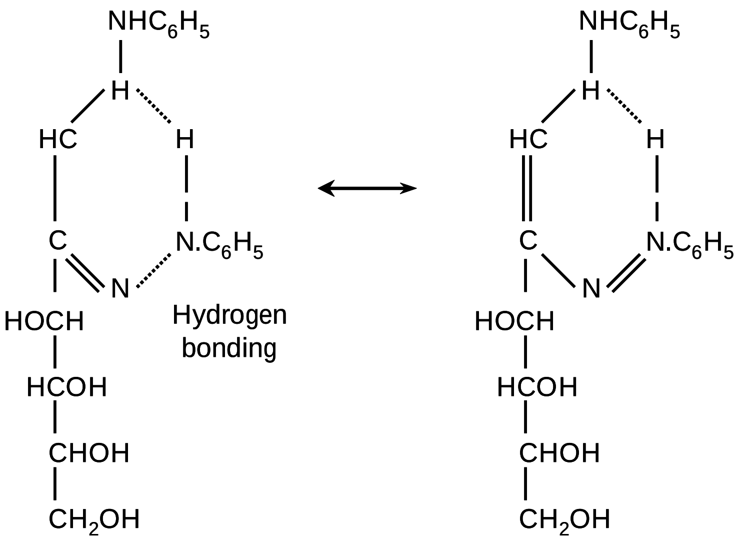


$$CH{=}N.NHC_6H_5-CHOH-(CHOH)_5-CH_2OH + C_6H_5NHNH_2 \longrightarrow CH{=}N.NHC_6H_5-CO-(CHOH)_5-CH_2OH + C_6H_5NH_2 + NH_3$$

3. The new keto group reacts with the third molecule of phenylhydrazine to form glucosazone.



$$CH{=}N.NHC_6H_5-C{=}O-(CHOH)_3-CH_2OH + H_2N.NHC_6H_5 \longrightarrow CH{=}N.NHC_6H_5-C{=}N.NHC_6H_5-(CHOH)_3-CH_2OH$$



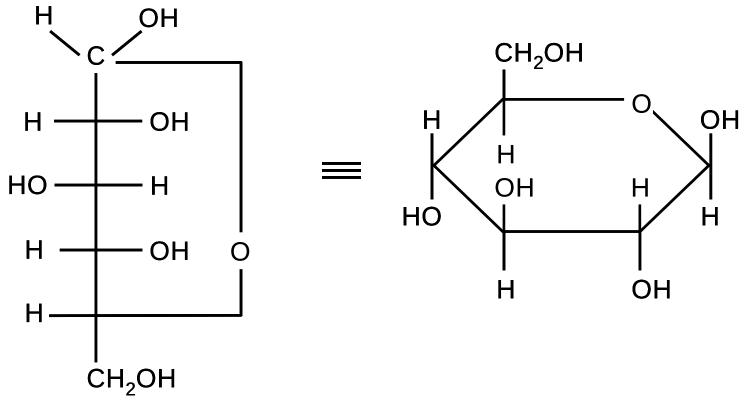
Q13. Write the Haworth Cyclic structures for glucose & fructose.

Ans : **(Imp.)**

Cyclic Structure of Glucose

Five and six membered rings in the structure of sugars are denoted by the terms Furanose and Pyranose e.g.: α – D – gluco pyranose and α – D – gluco furanose.

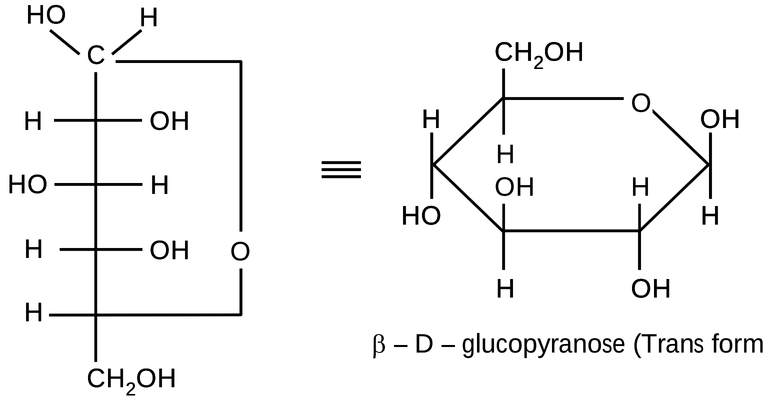
According to Haworth these formulae, may be written as more or less regular pentagons and hexagons.



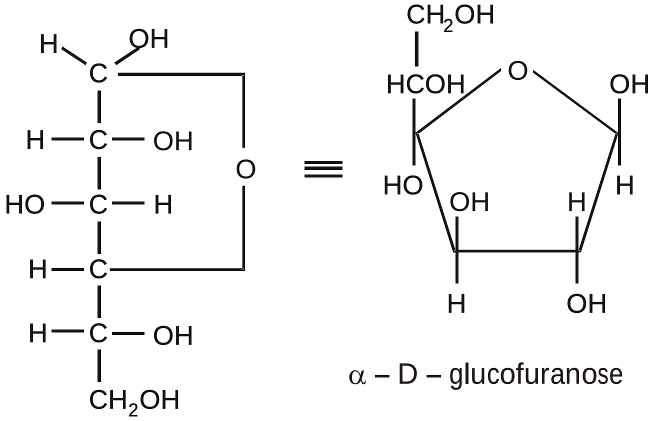
Fischer Structure

Haworth Structure

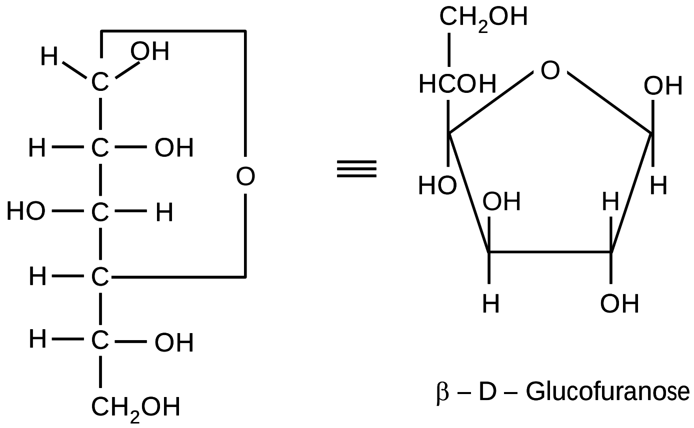
α – D – glucopyranose (cis form)



β – D – glucopyranose (Trans form)



α – D – glucofuranose



β – D – Glucofuranose

Q14. Explain the Kiliani - Fischer method.

OR

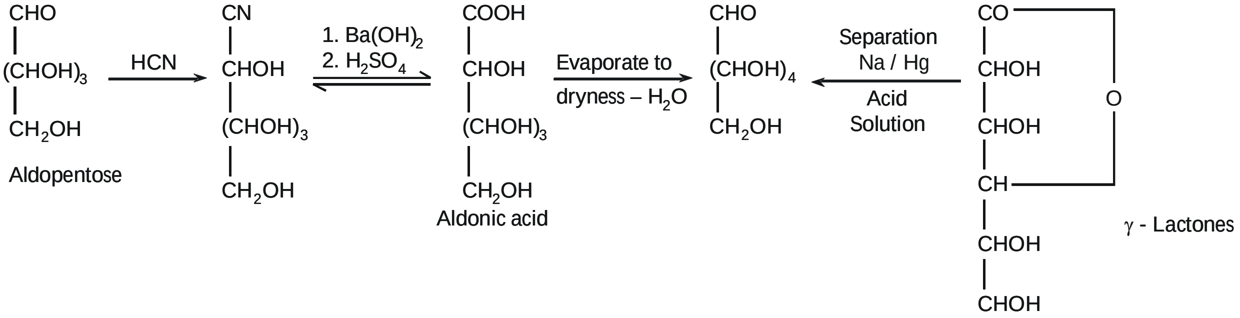
Write the conversion of aldopentose to aldohexose.

Ans :

Kiliani's Synthesis

Conversion of arabinose (aldopentose) to glucose (aldohexose).

1. The aldopentose is dissolved in dil HCN to form cyanohydrin.
2. The cynanohydrins are hydrolysed with aq $Ba(OH)_2$ yielding a mixture of two aldonic acids. Excess of $Ba(OH)_2$ is removed as insoluble $BaSO_4$ by the addition of calculated quantity of dil H_2SO_4.
3. The filtrate conaining aldonic acids is evaporated to dryness to give a mixture of two γ-lactones which are then separated by fractional crystallisation.
4. The γ - ketones are reduced in acidic medium to yield the corresponding aldose.



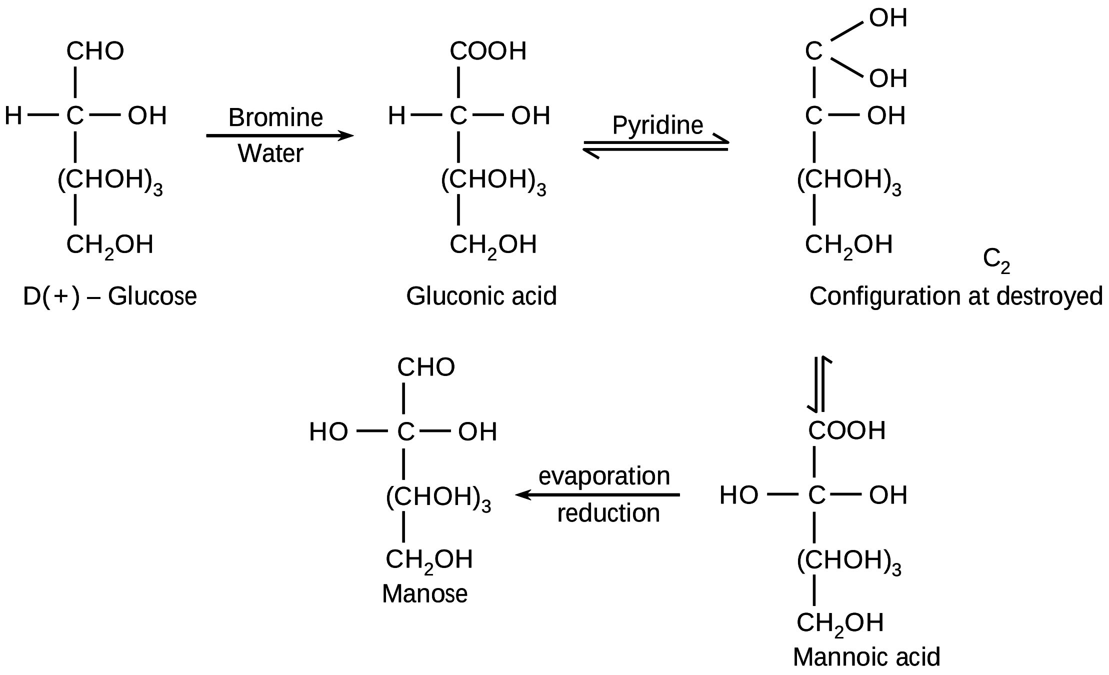
Q15. What are epimers. Explain the epimerisation process.

Ans :

Epimerisation

Compounds which differ only in the configuration at C_2 are called as epimers.

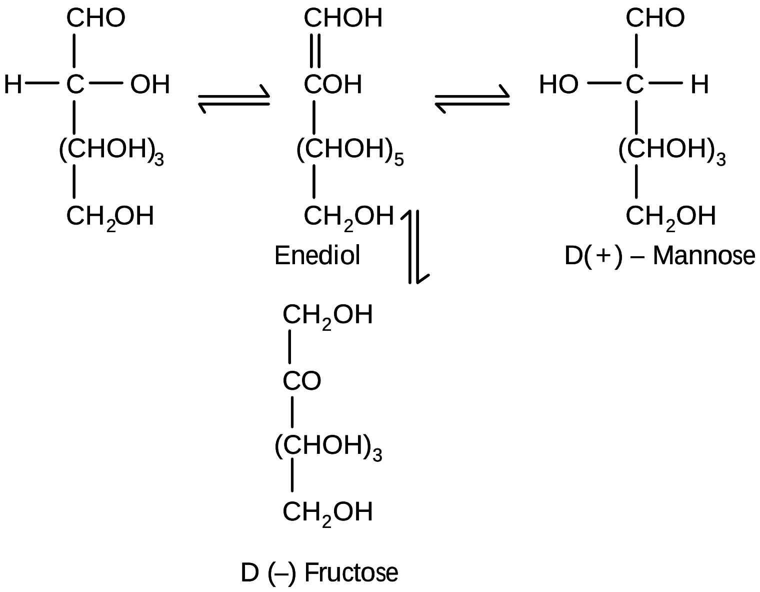
Epimers are the optical isomers which differ in the configuration at only one asymmetric carbon atom and the process of converting one epimer into other i.e., inversion of configuration at one asymmetric centre in a molecule containing several asymmetric centres is known as epimerisaiton.



Q16. Describe lobry de bruyn van ekenstein rearrangment.

Ans :

Glucose warmed with dil alkali solution is converted into a mixture of glucose, manose and fructose.



Q17. Explain the Ruff's degradation process.

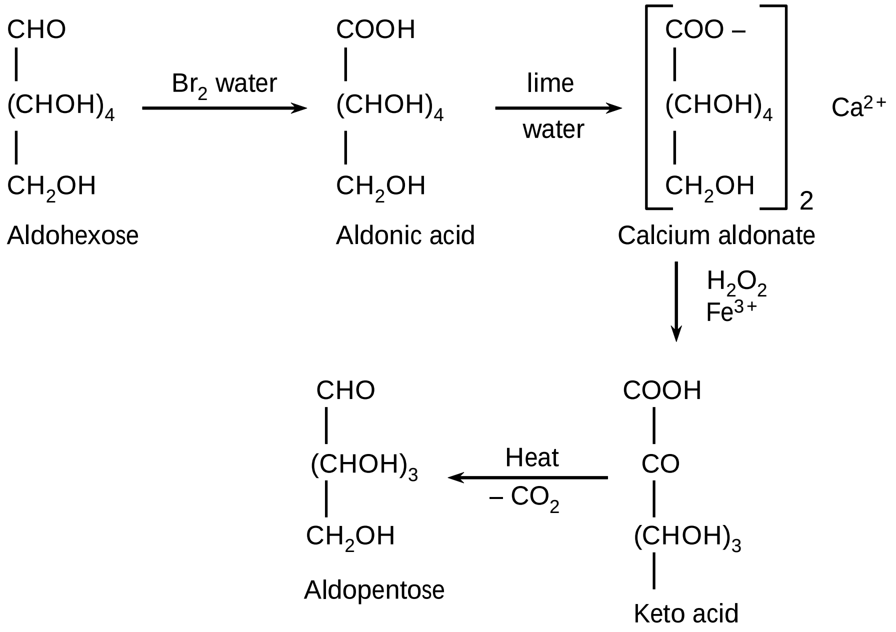
OR

Write the conversion of Aldohexose to Aldopentaose. (D-Glucose to D - Arabinose).

Ans :

Ruff's Degradation

1. The aldose is oxidised with bromine water to the corresponding aldonic acid.
2. The calcium salt of the aldonic acid is oxidised by hydrogen peroxide in presence of ferrous salt as a catalyst (Fenton's reagent H_2O_2 + Fe^{3+}) to the α - keto acid which is readily decarboxylated to the lower aldose.



$$\underset{\text{Aldohexose}}{\begin{matrix}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{matrix}} \xrightarrow{Br_2\text{ water}} \underset{\text{Aldonic acid}}{\begin{matrix}COOH\\|\\(CHOH)_4\\|\\CH_2OH\end{matrix}} \xrightarrow[\text{water}]{\text{lime}} \underset{\text{Calcium aldonate}}{\left[\begin{matrix}COO-\\|\\(CHOH)_4\\|\\CH_2OH\end{matrix}\right]_2 Ca^{2+}} \xrightarrow{H_2O_2,\ Fe^{3+}} \underset{\text{Keto acid}}{\begin{matrix}COOH\\|\\CO\\|\\(CHOH)_3\\|\end{matrix}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Aldopentose}}{\begin{matrix}CHO\\|\\(CHOH)_3\\|\\CH_2OH\end{matrix}}$$

Q18. Write the conversion of glucose to fructose.

OR

Aldohexose to ketohexose.

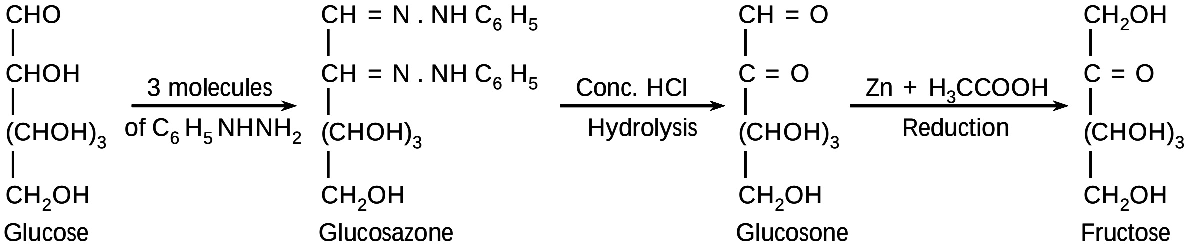
Ans :

(a) Conversion of an aldose into the corresponding ketose glucose into fructose.

A glucose is warmed with escess of phenylhydrazine to form glucosazone.

(b) Glucosazone is hydrolysed with conc. HCl to give glucosone (polyhydroxy ketoaldehyde).

(c) Glucosone when reduced with zinc and acetic acid gives fructose.



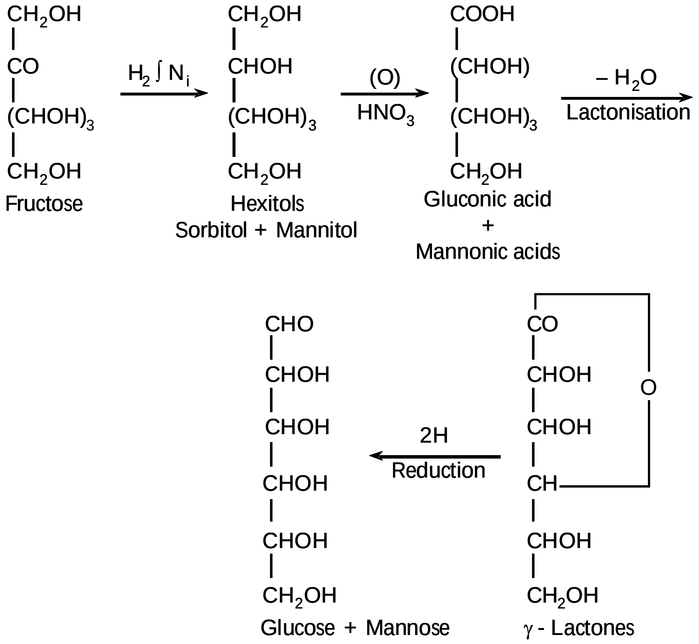
$$\underset{\text{Glucose}}{\begin{matrix}CHO\\|\\CHOH\\|\\(CHOH)_3\\|\\CH_2OH\end{matrix}} \xrightarrow[\text{of } C_6H_5NHNH_2]{\text{3 molecules}} \underset{\text{Glucosazone}}{\begin{matrix}CH = N\,.\,NH\,C_6\,H_5\\|\\CH = N\,.\,NH\,C_6\,H_5\\|\\(CHOH)_3\\|\\CH_2OH\end{matrix}} \xrightarrow[\text{Hydrolysis}]{\text{Conc. HCl}} \underset{\text{Glucosone}}{\begin{matrix}CH = O\\|\\C = O\\|\\(CHOH)_3\\|\\CH_2OH\end{matrix}} \xrightarrow[\text{Reduction}]{Zn + H_3CCOOH} \underset{\text{Fructose}}{\begin{matrix}CH_2OH\\|\\C = O\\|\\(CHOH)_3\\|\\CH_2OH\end{matrix}}$$

Q19. Write the conversion of Ketohexose to aldohexose.

Ans :

Conversion of a Ketose into the Corresponding Aldose Fructose into Glucose

1. Fructose is catalytically reduced to give a mixture of sorbitol and mannitol.
2. The mixture of the two hexitols is oxidised with nitric acid to form a mixture of hexonic acids. Which immediately lose molecule of water forming γ - lactones. γ - lactones are separated by fractional crystallisation.



S4-O-2: AMINO ACIDS AND PROTEINS

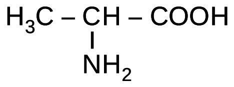
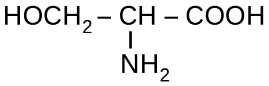
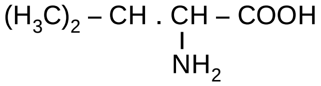
Q20. Write the classification of aminoacids with examples.

Ans : **(Imp.)**

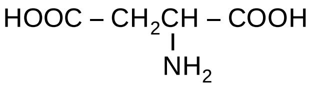
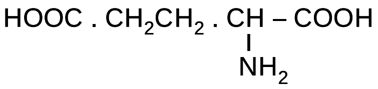
Classification of Natural Amino Acids

(a) Classification Based on Nature of Aminoacids

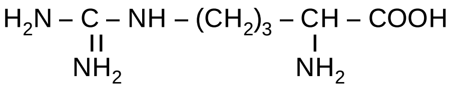
1. Neutral Amino Acids : These contain one amino and one carboxyl groups.

Name	Abbreviation	Group Formula
Glycine	Gly	H_2N-CH_2-COOH
Alanine	Ala	 $H_3C-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-COOH$
Serine	Ser	 $HOCH_2-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-COOH$
Valine	Val	 $(H_3C)_2-CH\,.\,\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-COOH$

2. **Acidic Amino Acids :** These contain one amino and two carboxyl groups.

Name	Abbreviation	Formula
Aspartic acid	Asp	 $HOOC - CH_2\underset{\underset{NH_2}{\vert}}{CH} - COOH$
Glutanic acid	Glu	 $HOOC \,.\, CH_2CH_2 \,.\, \underset{\underset{NH_2}{\vert}}{CH} - COOH$

3. **Basic Amino Acids :** These contain two amino and one carboxyl groups.

Name	Abbreviation	Formula
Lysine	Lys	$H_2N(CH_2)_4 \,.\, CH(NH_2) \,.\, COOH$
Arginine	Arg	 $H_2N - \underset{\underset{NH_2}{\Vert}}{C} - NH - (CH_2)_3 - \underset{\underset{NH_2}{\vert}}{CH} - COOH$

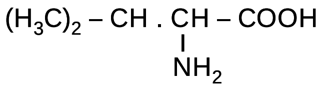
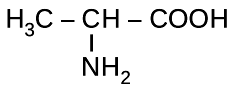
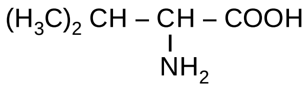
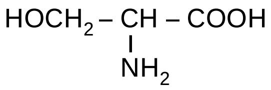
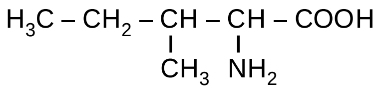
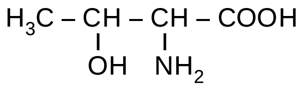
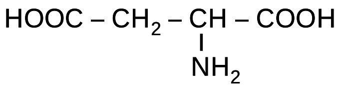
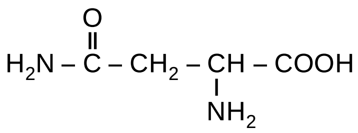
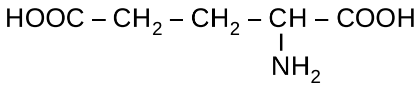
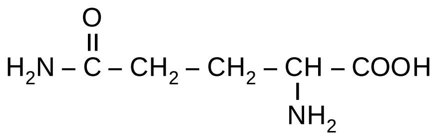
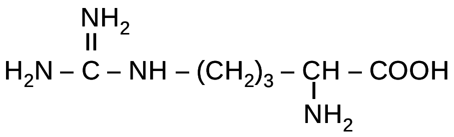
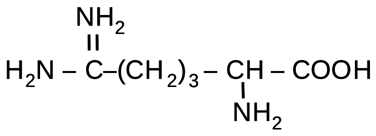
(b) Classification Based on Function of Amino Acids

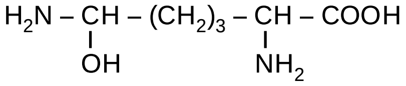
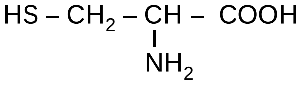
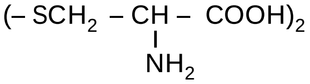
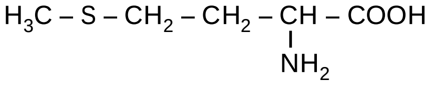
Among the 25 known (natural) aminoacids certain amino acids may be synthesized in the body. Some cannot be synthesized in the body at a rate necessary for normal growth and they must be supplied in the diet. Therefore the first category of aminoacids are called dispensable or nonessential amino acids. Second category are known as indispensable or essential amino acids. Deficiency of amino acid prevents growth in young animals and may even cause death. There are ten amino acids that are essential to man. Arginine and histidine are less important.

Ten Important α - amino acids

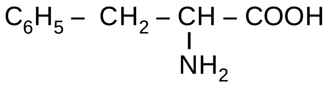
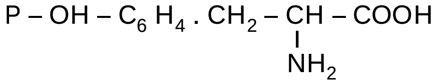
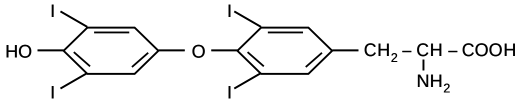
1. Threonine - Thr
2. Valine - Val
3. Leucine - Leu
4. Isoleucine - Ileu
5. Lysine - Lys
6. Methione - Met
7. Phenylalanine - Phe
8. Tryptophan - Trp
9. Arginine - Arg
10. Histidine - His

1. Aliphatic Amino Acids

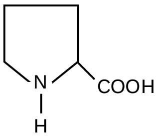
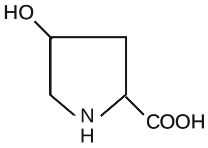
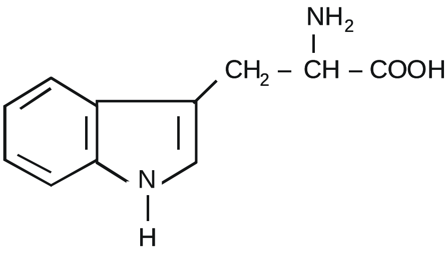
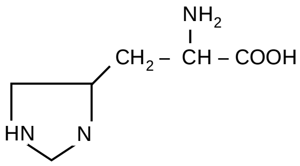
Glycine	Gly	$H_2N - CH_2 - COOH$
Valine	Val	 $(H_3C)_2 - CH \,.\, \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Alanine	Ala	 $H_3C - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Leucine	Leu	 $(H_3C)_2\, CH - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Serine	Ser	 $HOCH_2 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Isoleucine	Ileu	 $H_3C - CH_2 - \underset{\substack{\vert \\ CH_3}}{CH} - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Threonine	Thr	 $H_3C - \underset{\substack{\vert \\ OH}}{CH} - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Aspartic acid	Asp	 $HOOC - CH_2 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Asparagine	Asp – NH_2(or) (Asn)	 $H_2N - \overset{\substack{O \\ \Vert}}{C} - CH_2 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Glutamic acid	Glu	 $HOOC - CH_2 - CH_2 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Glutamine	Glu – NH_2 (or) Gln	 $H_2N - \overset{\substack{O \\ \Vert}}{C} - CH_2 - CH_2 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Arginine	Arg	 $H_2N - \overset{\substack{NH_2 \\ \Vert}}{C} - NH - (CH_2)_3 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$
Lysine	Lys	 $H_2N - \overset{\substack{NH_2 \\ \Vert}}{C} - (CH_2)_3 - \underset{\substack{\vert \\ NH_2}}{CH} - COOH$

Hydroxylysine	Lys – OH	 $H_2N-\underset{OH}{\underset{\mid}{CH}}-(CH_2)_3-\underset{NH_2}{\underset{\mid}{CH}}-COOH$
Cysteine	Cys	 $HS-CH_2-\underset{NH_2}{\underset{\mid}{CH}}-COOH$
Cystine	Cysy	 $(-SCH_2-\underset{NH_2}{\underset{\mid}{CH}}-COOH)_2$
Methionine	Met	 $H_3C-S-CH_2-CH_2-\underset{NH_2}{\underset{\mid}{CH}}-COOH$

Aromatic Amino Acid

Phenylalanin	Phe	 $C_6H_5-CH_2-\underset{NH_2}{\underset{\mid}{CH}}-COOH$
Tyrosine	Tyr	 $P-OH-C_6H_4.CH_2-\underset{NH_2}{\underset{\mid}{CH}}-COOH$
Thyroxine	Thy	

Heterocyclic Amino Acids

Proline	Pro	
Hydroxyproline	Hypro	
Tryptophan	Try	
Histidine	His	

Q21. Write the General Preparation Methods of Aminoacids ?

Ans :

Synthesis of α – Amino Acids

1. Amination of α - Halogen Acids

An α - Halogenated Acid is treated with a large excess of ammonia.

$$Cl-CH_2-COOH + 3NH_3 \xrightarrow{-NH_4Cl} H_2N-CH_2-COONH_4 \xrightarrow{-H^+} \underset{\text{Glycine}}{H_2N-CH_2-COOH}$$

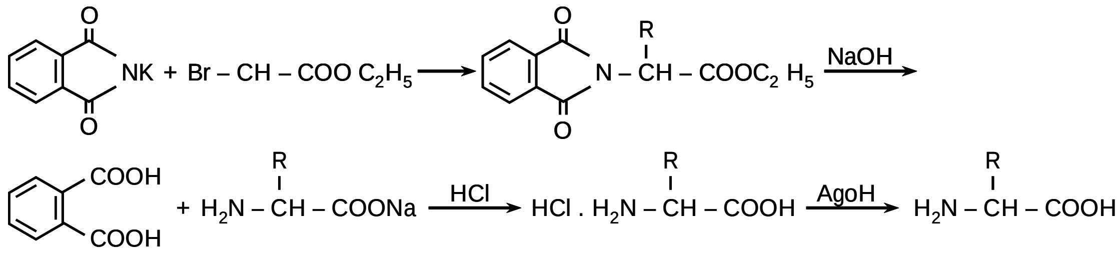
α – Halogenated acids are more easily obtained by treating aliphatic carboxylic acids with chlorine or bromine in the presence of a small amount of phosphorus. In this reaction only α - hydrogen atom is replaced by halogen. The reaction is known as Hell-Volhard Zelinsky reaction.

$$H_3C-COOH \xrightarrow{Cl_2\ h\nu} \underset{\text{Chloroacetic acid}}{Cl-CH_2-COOH}$$

Glycine, alanine, serine, threonine, valine, leucine have been prepared by this method.

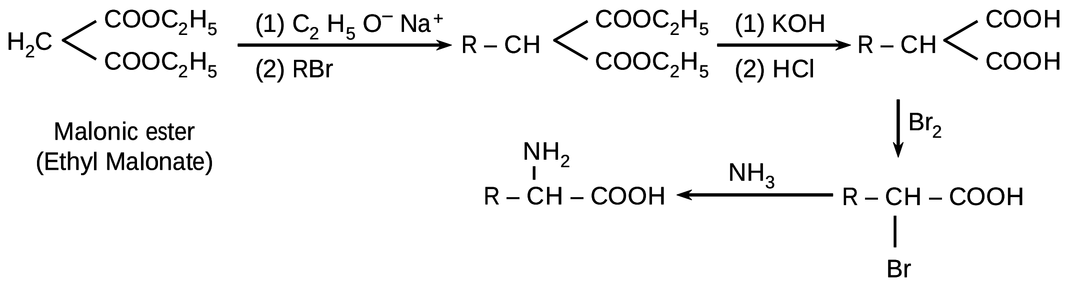
2. Garbriel Phthalimide Synthesis

An α – halogenated acid - ester is treated with potassium phthalimide to form a substituted phthalimide which on hydrolysis gives phthalic acid and an aminoacid.



3. Malonic Ester Synthesis

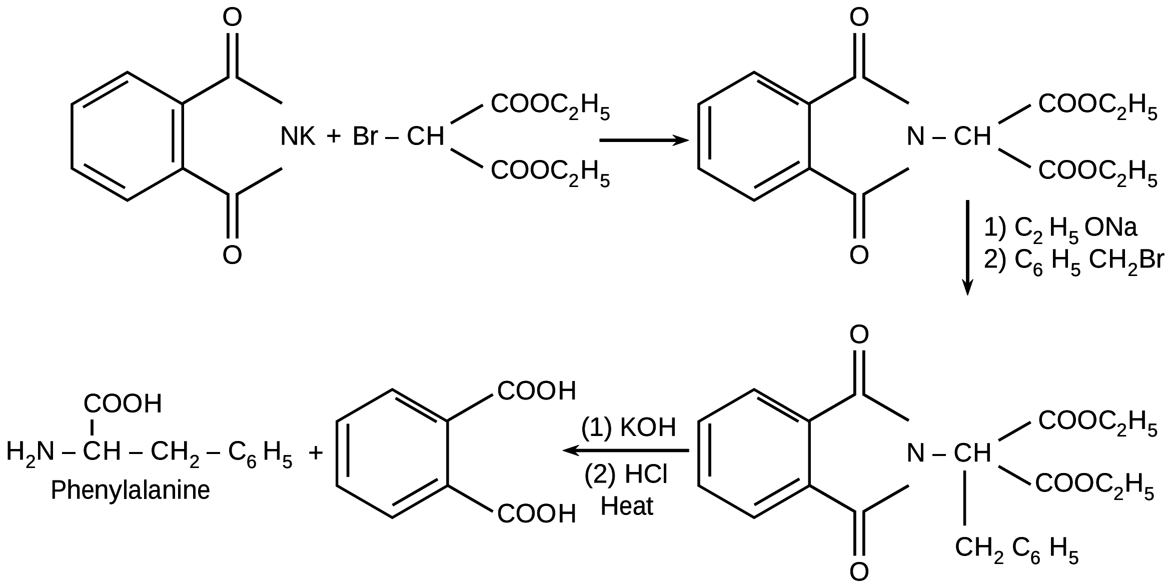
This method is really an extension of method No.1.



This method offering phenylalanine, Proline, Leucine, Isoleucine and Methionine.

4. Phthalimidomalonic Ester Synthesis

This method is a combination of malonic ester synthesis and Gabriel pthalimide synthesis. In this method phthalimidomalonic ester is treated with the appropriate alkylchloride in the presence of sodium ethoxide and the product is hydrolysed to yield the aminoacid. Phenyl alanine, cystine, tyrosine, proline, serine, aspartic acid, lysine and methionine have been synthesised by this method.

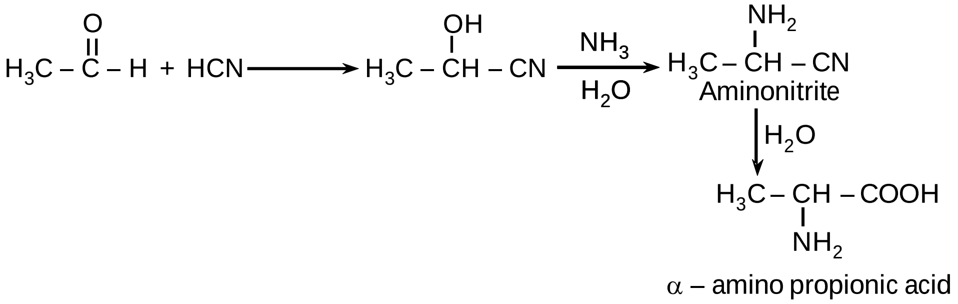


5. Strecker's Synthesis

An aldehyde (or) ketone is treated with a mixture of ammonium chloride and sodium cyanide to form cyanorydrin which on hydrolysis give the corresponding aminoacid.

$NH_4Cl + NaCN \longrightarrow NH_4CN + NaCl$

$NH_4CN \longrightarrow NH_3 + HCN$



Q22. Write the physical properties of aminoacids.

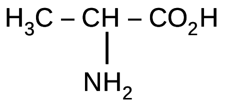
Ans :

1. Aminoacids are colourless, crystalline substances having sweet taste. They melt with decomposition at high temperature.
2. They are solube in polar solvents like water and insoluble in organic solvents such as ether.
3. Water solutions are neutral to litmus owing to the formation of their internal salt or zwitter ion.

Q23. Write the optically active aminoacids.

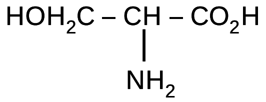
Ans :

Alanine



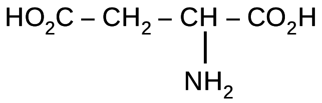
$H_3C-CH(NH_2)-CO_2H$

Serine



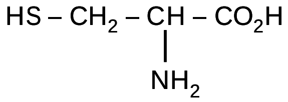
$HOH_2C-CH(NH_2)-CO_2H$

Asparticacid



$HO_2C-CH_2-CH(NH_2)-CO_2H$

Cysteine



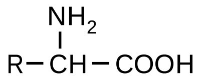
$HS-CH_2-CH(NH_2)-CO_2H$

Q24. What is zwitter ion & write its characteristics.

Ans :

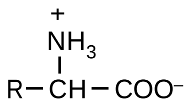
Zwitter Ion

Due to the presence of an acidic and basic are neutral and exist as dipolar or zwitter ions or inner salts in which proton from the carboxyl group has been transferred to the amino group a dipolar ion containing both a positive and a negative charge is formed.



$R-CH(NH_2)-COOH$

Aminoacid



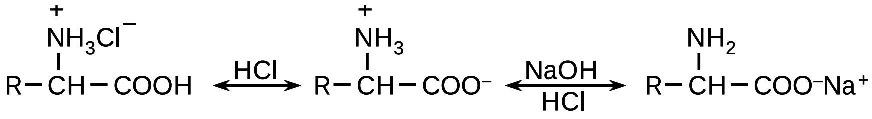
$R-CH(\overset{+}{N}H_3)-COO^-$

Zwitter ion

The presence of dipolar ion structure of aminoacids is evidenced by the following points.

1. The high melting or decomposition point and the solubility in water, and insolubility in ether and other organic solvents.
2. Solution of aminoacids have very high dielectric constant.
3. The spectroscopic studies show the absence of the characteristic vibration frequencies for the free carboxyl and amino groups.
4. It explains the different electrolytic behaviour of the amino acids in different media.

   E.g. In an acidic solution an amino acid behaves as protonated derivative and migrates to the cathode. In alkaline medium the same amino acid behaves as anion and migrates to the anode.



$$R-CH(\overset{+}{N}H_3\overset{-}{Cl})-COOH \xleftrightarrow{HCl} R-CH(\overset{+}{N}H_3)-COO^- \underset{HCl}{\overset{NaOH}{\longleftrightarrow}} R-CH(NH_2)-COO^-Na^+$$

Cation (Migrates to cathodes) Zwitter ion Anion (Migrates to anode)

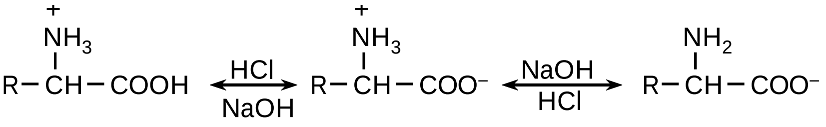
5. Titration of amino acid with base involves neutralization of the $\overset{+}{N}H_3$ group and not the – COOH group. Similarly titration of an amino acid with acid neutralizes the $-COO^-$ group of the amino acid and not its $-NH_2$ group.

Q25. Define isoelectric point.

Ans : **(Imp.)**

Isoelectric Point

The addition of a proton to an aminoacid converts it into a cation while the addition of a base converts it into an anion. At a definite pH value, the acidic and basic properties of the amino acid must be balanced and the aminoacid at this particular pH should exist as a neutral dipolar ion (i.e., electrically neutral zwitter ion).



$$R-\overset{\overset{+}{N}H_3}{CH}-COOH \underset{NaOH}{\overset{HCl}{\rightleftharpoons}} R-\overset{\overset{+}{N}H_3}{CH}-COO^- \underset{HCl}{\overset{NaOH}{\rightleftharpoons}} R-\overset{NH_2}{CH}-COO^-$$

Cation-III Zwitter ion I Anion II

At a particular pH there is no net charge on the aminoacid moleculer and which thus doesnot migrate to any electrode under the influence of electric current is known as isoelectric point. The isoelectric point of each aminoacid is constant. An amino acid at pH values lower than that of its isoelectric point exists mainly as the anion II. At pH values higher than that of its isoelectric point it exists mainly as the cation III. The isoelectric point characteristic of the aminoacids is the basis of the process.

Mono amino mono carboxylic acids have isoelectric point of the order of 6. It is less than 6 in case of mono amino dicarboxylic acids and more than 6 in case of diamino monocarboxylic acids.

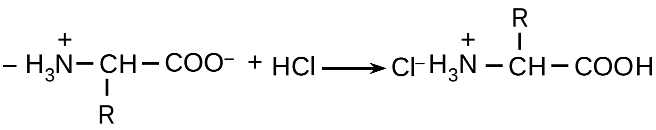
An aminoacid has the maximum solubility at its isoelectric point.

Q26. Write the chemical properties of amino acids.

Ans :

Chemical Properties of Aminoacids

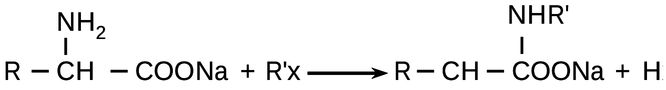
Reactions of the amino groups : Action with mineral acid : Amino acids form salts on treatment with mineral acids.



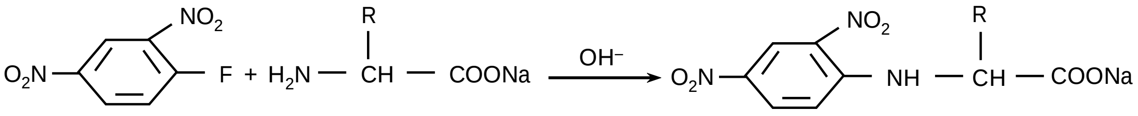
$$-H_3\overset{+}{N}-\underset{R}{CH}-COO^- + HCl \longrightarrow Cl^-H_3\overset{+}{N}-\overset{R}{CH}-COOH$$

Alkylation

Amino acids in alkaline solution react with alkylhalides to form N-alkyl substituted amino acids.



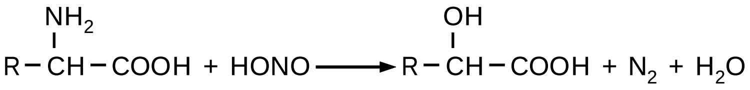
$$R-\overset{\overset{NH_2}{|}}{CH}-COONa + R'x \longrightarrow R-\overset{\overset{NHR'}{|}}{CH}-COONa + H$$



2.4-Dinitro fluro benzene Sanger’s reagent/2,4-DNF

Reaction with nitrous Acid

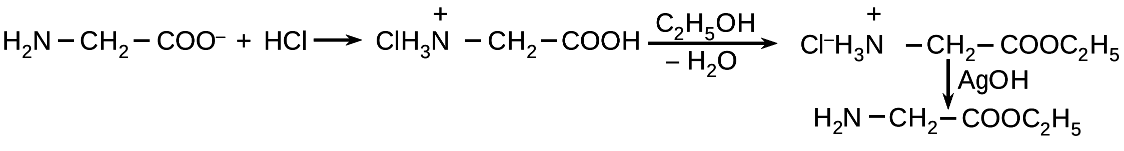
α-Amino acids react with nitrous acid to give α-hydroxy acid and nitrogen.



$$R-\overset{\overset{NH_2}{|}}{CH}-COOH + HONO \longrightarrow R-\overset{\overset{OH}{|}}{CH}-COOH + N_2 + H_2O$$

Reaction of Carbonylic Group

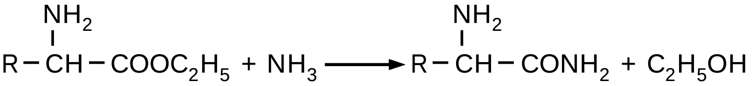
1. Esterification



$$H_2N-CH_2-COO^- + HCl \longrightarrow ClH_3\overset{+}{N}-CH_2-COOH \xrightarrow[-H_2O]{C_2H_5OH} Cl^-H_3\overset{+}{N}-CH_2-COOC_2H_5 \xrightarrow{AgOH} H_2N-CH_2-COOC_2H_5$$

Ester

2. Reaction with Ammonia



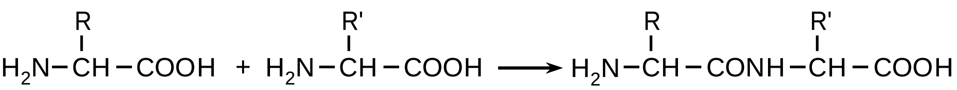
$$R-\overset{\overset{NH_2}{|}}{CH}-COOC_2H_5 + NH_3 \longrightarrow R-\overset{\overset{NH_2}{|}}{CH}-CONH_2 + C_2H_5OH$$

Q27. What is peptide bond.

Ans :

Peptide

Peptide as a substance derived from two (or) more amino acids and united through peptide bonds.



$$H_2N-\overset{\overset{R}{|}}{CH}-COOH + H_2N-\overset{\overset{R'}{|}}{CH}-COOH \longrightarrow H_2N-\overset{\overset{R}{|}}{CH}-CONH-\overset{\overset{R'}{|}}{CH}-COOH$$

Q28. Write the nomenclature of peptides proteins.

Ans :

Classification of Proteins

Proteins are classified either by ‘chemical composition’ or by ‘molecular shape’.

Classification by Chemical Composition

According to this system, proteins are divided into two classes.

1. **Simple Proteins.** The simple proteins are those which are made of chains of amino acid units only, joined by amide linkages. Upon hydrolysis, they yield mixtures of amino acids Examples are:

Albumins : Egg albumin, serum albumin, lact albumin.

Globulins : Tissue globulin, serum globulin.

Glutenins : Glutenin in wheat, coryzenin in rice.

2. **Conjugated Proteins.** These molecules are made up of a simple protein united covalently or non-covalently with a non-protein factor. The non-protein portion is called a prosthetic group (Gr. prosthesis = an addition) or Cofactor. Examples are:

Glycoproteins : Mucin in saliva ; prosthetic group, carbohydrate.

Phosphoproteins : Casein in milk ; prosthetic group, phosphoric acid.

Chromoproteins : Hemoglobin in red blood cells ; prosthetic group, coloured iron pigment.

Classification by Molecular Shape

This shape-classification divides proteins into two types depending on their molecular shape:

(i) Fibrous proteins, which are fibre-like; (ii) Globular proteins, which are globe-like or spherical.

1. **Fibrous Proteins.** In these proteins, the polypeptide chains coil about one another and are held together by strong inter-chain hydrogen bonds (between H and O of amino acid units of different chains). Thus their molecules assume the shape of large linear fibres which are used for connections, support, and the structure in living organisms. They are insoluble in water. Examples are :

Keratin : Present in skin, hair and nails.

Myosin : Present in muscles.

Collagen : Present in tendons, cartilages and bones.

2. **Globular Proteins.** Their molecules are globular or roughly spherical in shape. They are made of polypeptide chains coiled back and fold on themselves so as to make compact spheroid molecules. The polypeptide chains are held together firmly by intra-chain hydrogen bonds (between H and O of amino acid units of same chain). Globular proteins are generally soluble in water, or solutions of acids, bases, and salts.

The function of the globular proteins is to maintain and regulate life processes in the living organisms. Examples are:

Enzymes : Pepsin from stomach ; helps digestion.

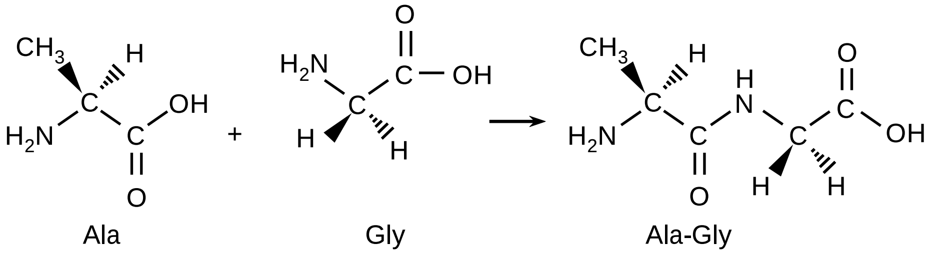
Insuline : Secreted by pancreas ; regulates glucose metabolism.

Hemoglobin : Present in blood ; transports O_2 from lungs to all cellular tissues.

Antibodies : Protect the body from outside infection e.g., gama globulin in blood.

Cytochromes : Present in blood ; act as electron carriers.

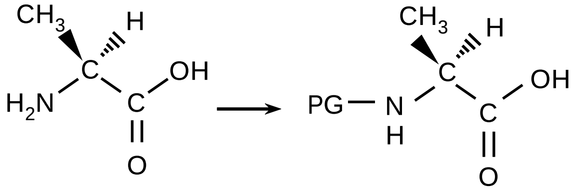
Q29. Write about peptide synthesis. Synthesis of Ala-Gly from alanine and glycine.



Ans :

Step I

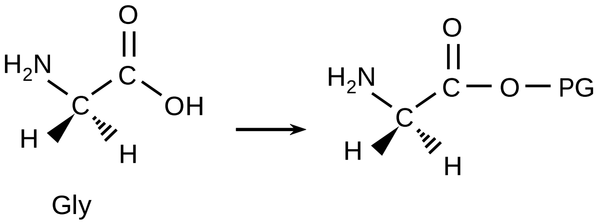
Protect the NH_2 gp of alanine.



P_g = Protecting group

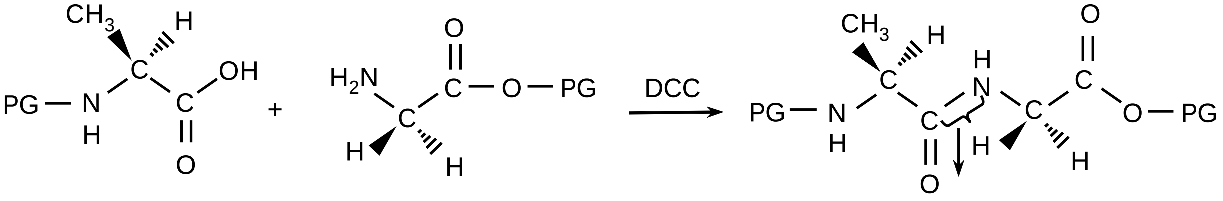
Step II

Protect the COOH group of glycine



Step III

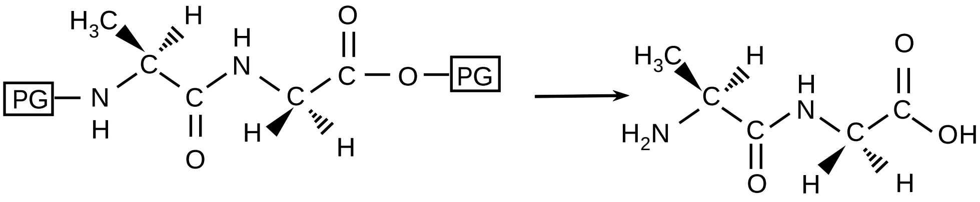
Form the amide bond with DCC.



DCC - Dicyclohexyl carbodimide is a reagent commonly new amide bond used to form amide bands. DCC makes the OH group of COOH a better leaving group & thus activating the – COOH. group toward nucleophilic attack.

Step IV

Remove one or both protecting groups.



Ala-Gly

S4-O-3: HETEROCYCLIC COMPOUNDS

Q30. Define heterocyclic campounds with examples.

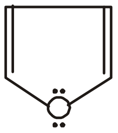
Ans :

The cyclic organic compounds in which one (or) more carbon atoms organic of the ring have been placed by other atoms such as Nitrogen, Oxygen, Sulfer are called heterocyclic compounds.

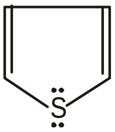
1. **Five Membered Heterocyclic**

These contain five atoms in the ring including the heteroatom(N,O,S)

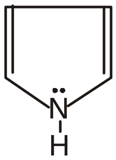
Examples :



Furan



Thiophene

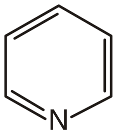


Pyrrole

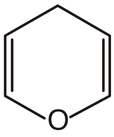
2. **Six Membered Heterocyclic**

These contain six atoms in the ring including the heteroatom (N, O, S)

Examples :



Pyridine



Pyran

Q31. Write the numbering of heterocyclic systems as per greek letter and numbers.

Ans :

According to IUPAC system of nomenclature, the names of the heterocyclic compounds are made up of three parts.

(i) a prefect that describes the heteoatom

eg., oxa for O

aza for N

thia for S

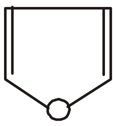
(ii) a stem - that indicates the ring size

eg., – ol – for 5 membered ring

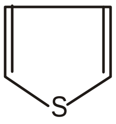
– in – for 6 membered ring

(iii) a suffix that indicates ring saturation or unsaturation

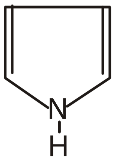
Thus, the IUPAC name for furan, thiophene, pyrrole are given below in bracket



Furan(oxaole)



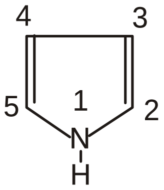
Thiophene(Thiole)



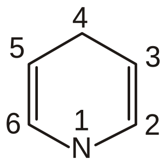
Pyrrole(Azole)

The ring positions are designated by numerals or Greek letters.

The numeral system the heteroatom is given number 1(or lowest number) and the numbering is continued in anti-clockwise direction.



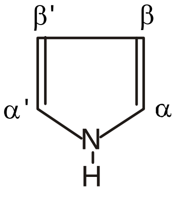
Pyrrole

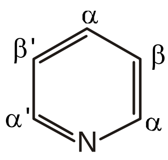


Pyridine

In Greek system, the position next to hetero atom is designated as α - followed by β - and so on.

eg.,





Q32. Explain the aromaticity and resonance structures of the following.

- **(a) Pyrrole**
- **(b) Thiophene**
- **(c) Furan**

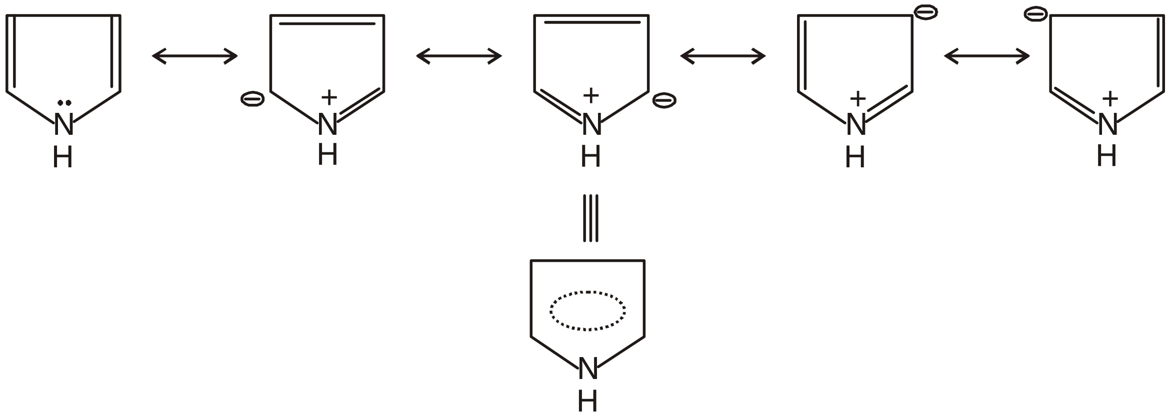
Ans : **(Imp.)**

(a) Aromaticity in Pyrrole

In pyrrole, the four, carbon atoms and the nitrogen atom are sp^2 hybridised. Each carbon has three sp^2 hybrid orbitals with an unpaired electron and an unhybridised p-orbital similarly, the nitrogen atom has three sp^2 hybrid orbitals with one lone pair of electrons and an unhybridised p-orbital. The carbon and nitrogen atom form C – H(sp^2 - s overlapping) C – C(sp^2 - sp^2), C – N(sp^2 - sp^2) and N – H (sp^2-s overlapping) σ bonds. The remaining p-orbital with 1 electron on each carbon and a p-orbital with 2 electrons on the nitrogen atom the five orbitals are parallel to each other and overlaps sideways to form a cyclic detocalised π - molecular orbital containing 6 electrons(aromatic sextet i.e., 1 lone pair + 4 single $\bar{e}$ = $6\pi\bar{e}$ s) in cylic ring system

The sextet of delocalised $\pi\bar{e}$'s, Huckel's rule ($4n + 2\pi\bar{e}$'s) imports aromatic character to pyrrole

Resonance structures of Pyrrole

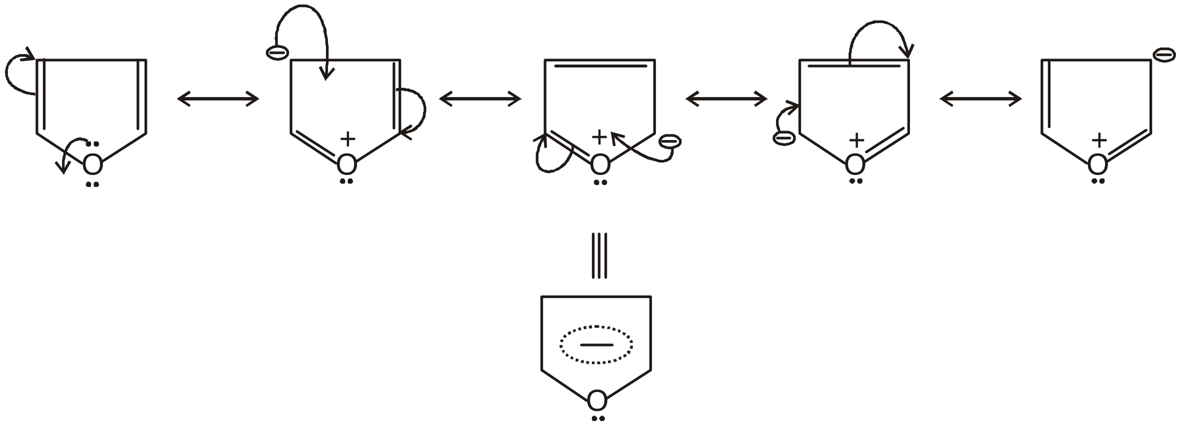


Aromaticity in Furan

In furan the 4 carbons and oxygen are all sp^2 hybridized oxygen uses its sp^2 hybrid orbitals in making two O – C bonds. The third sp^2 hybrid orbital carries an unshared pair of $\bar{e}$'s. The pure p-orbital on oxygen lies in the same plane as p-orbitals of carbon and carries a pair of e^-s. Overlap of five π- orbitals results in delocalisation of six $\pi\bar{e}$'s(1 lone pair + 4 single $\bar{e}$'s). The sexlet of delocatized $\pi\bar{e}$'s.

Huckel's rule ($4n + 2\pi\bar{e}$'s) imports aromatic character to furan.

Resonance structures of furan

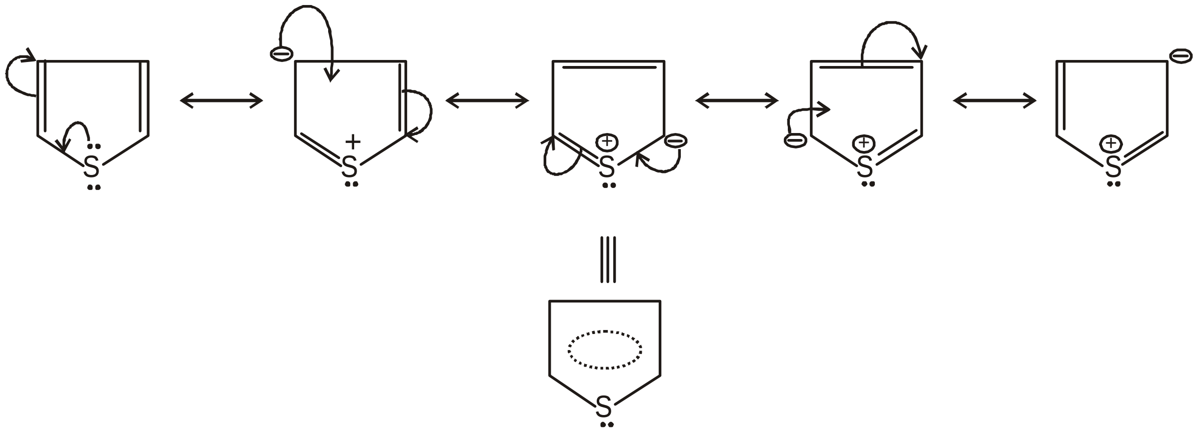


Aromaticity in Thiophene

In thiophene the carbons and sulphur all are sp^2 hybrized sulphur uses its sp^2 hybrid orbitals in making two S – C bonds. The third sp^2 hybrid orbital carries an unshared pair of $\bar{e}$'s. The pure p-orbital on sulphur lies in the same plane as p-orbitals of carbon and carries a pair of $\bar{e}$'s. Overlap of five π - orbitals results in delocalisation of six π - $\bar{e}$'s(1 lone pair + 4 single $\bar{e}$'s = $6\pi\bar{e}$'s). The sextet of delocalised $\pi\bar{e}$'s.

Huckel's rule ($4n + 2\pi\bar{e}$'s) imparts aromatic character to thiophene.

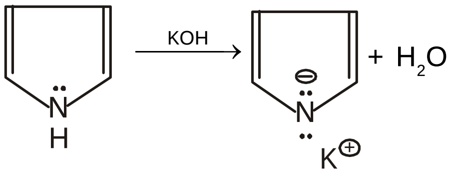
Resonance structures of Thiophene



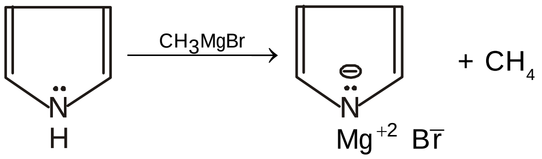
Q33. Explain the acidic character of pyrrole?

Ans : **(Imp.)**

Pyrrole is weakly acidic and forms alkali metal salts.



The acidic nature of pyrrole is supported by Grigrard reagent to form salt like magnesium halides.



The acidic character of pyrrole can be explained on the basis of following two facts :

(i) The lone pair of electrons of nitrogen is involved more in the formation of the sextet hence hydrogen is less firmly held by nitrogen. So, it can be removed easily as proton.

(ii) Once pyrryl anion is formed, it is resonance stabilised pyrryl anion is much more resonance stabilised than pyrrole itself.

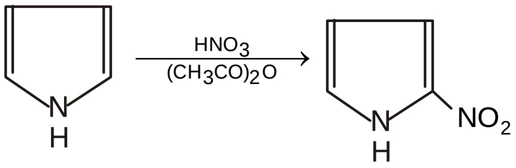
Q34. Write any three electrophilic substitution reactions of pyrrole, furan and thiophene.

Ans : **(Imp.)**

I. Pyrrole

(i) Nitration :

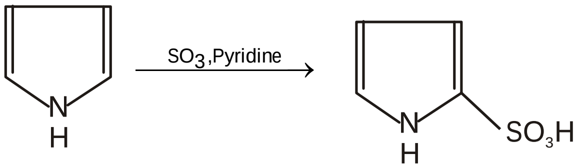
Nitration of pyrrole is carried out at low temperature in presence of nitric acid and acetic anhydride.



2-Nitropyrrole

(ii) Sulphonation

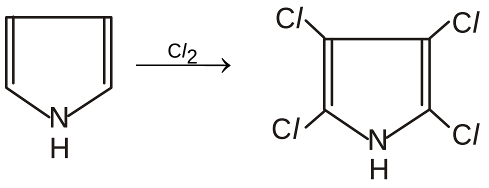
Sulphonation of pyrrole is carried out with sulphur trioxide



pyrrole-2-sulphonic acid

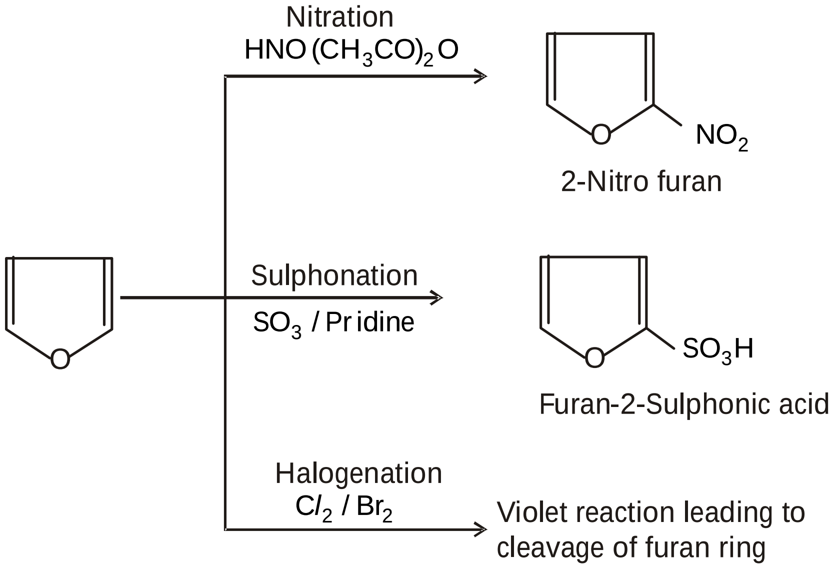
(iii) Halogenation

Pyrrole is highly reactive on halogenation results in the formation of 2, 3, 4, 5 - Tetrachloro pyrrole.

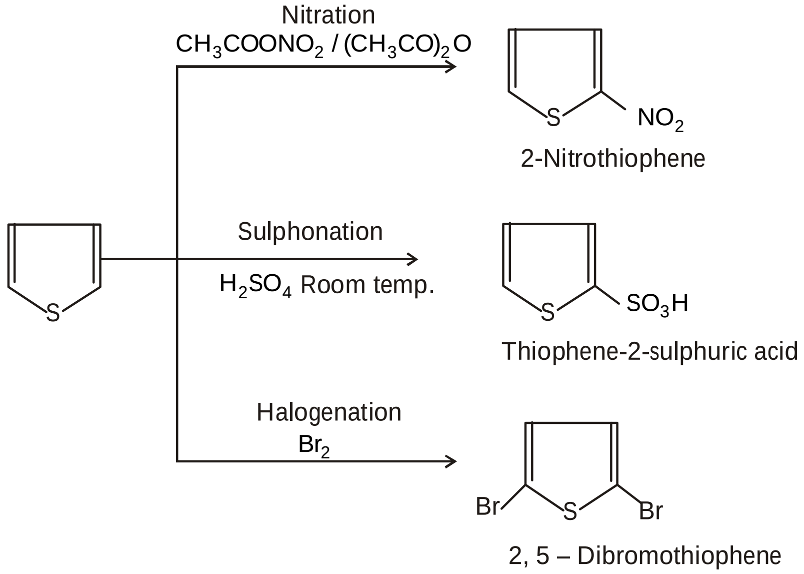


2, 3, 4, 5 - Tetra chloro pyrrole

II. Furan



III. Thiophene

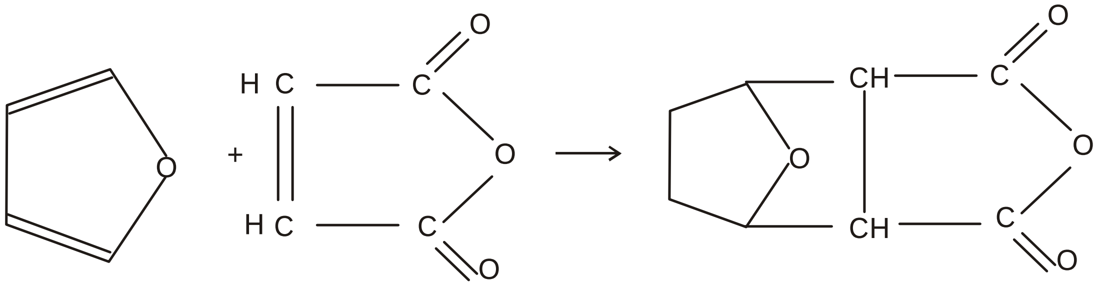


Reactivity of furan as 1,3-diene, Diel's Alder reaction (one example)

Q35. Give the Diel's Alser reaction of furan.

Ans :

Furan being least aromatic acts as a diene and reacts with maleicanhydride(dienophile) to form an adduct.



Furan (Diene) Maleic anhydride (Dienophile) Adduct

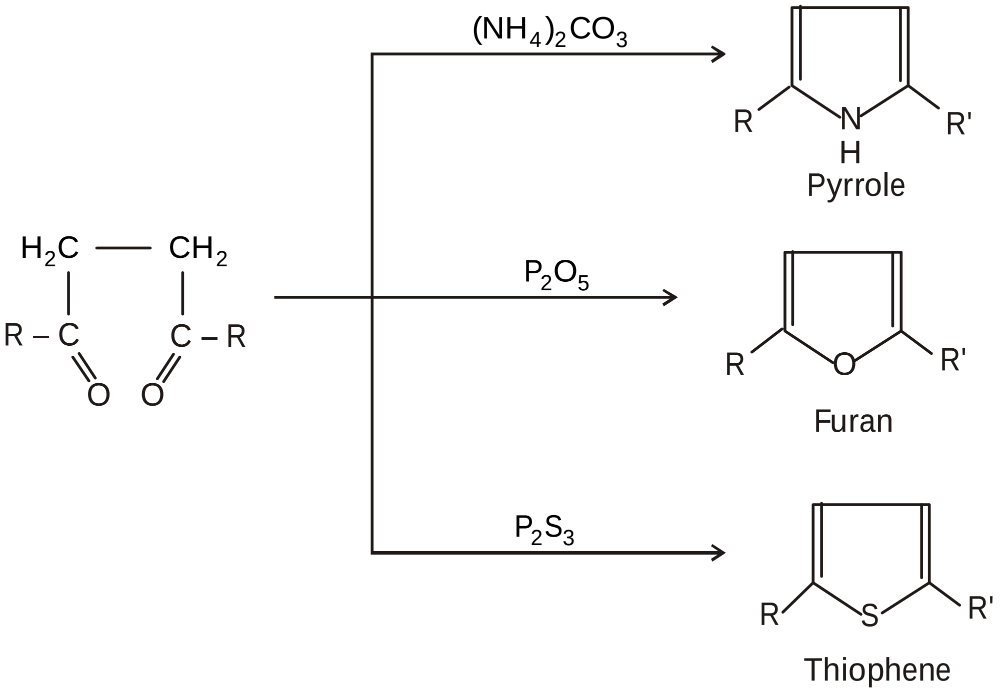
Q36. Write the Preparation of Pyrrole, furan, thiophene by Paul knorr synthesis.

Ans :

Heating of 1, 4- dicarbonyl compounds in presence of ammonium $(NH_4)_2CO_3$ carbonate gives rise to Pyrrole.

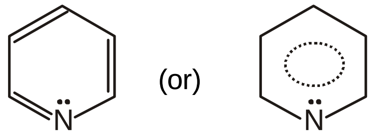
Heating of 1,4-dicarbonyl compounds in presence of phosphorous (P_2O_5) pentoxide gives rise to furan.

Heating of 1,4 - dicarbonyl compounds in presence of phosphorous (P_2S_3) trisulfide gives rise to Thiophene.



Q37. Explain the structure of pyridine.

Ans :



Pyridine is a heterocyclic compound with five carbon atom and a nitrogen atom with one lone pair of electrons.

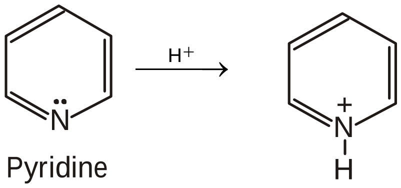
(i) The four carbon carbon bonds are equal in length (139 pm) and both the carbon nitrogen bonds are also equal in length (137 pm). These values are intermediate between the corresponding single and double bonds.

(ii) The stabilisation energy (125.5 kJ mol^{-1}) is greater than conjugated trienes.

Q38. Compare the basicity of pyridine with pyrrole.

Ans :

Pyridine is basic in nature because of the presence of lone pair of electrons on nitrogen. This lone pair doesnot participate in delocalisation and is readily available for reaction. Pyridine behaves as a typical tertiary amine. In acidic medium it form pyridinium salts.



Pyridine

Pyridinium salt

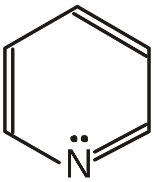
Pyrrole : In case of pyrrole the lone pair of electrons on nitrogen participates in delocalisation and forms a part of aromatic sextet. Due to non-availability of lone pair of electrons for reactions, pyrrole behaves as a weak base.

Q39. Describe the aromaticity of pyridine.

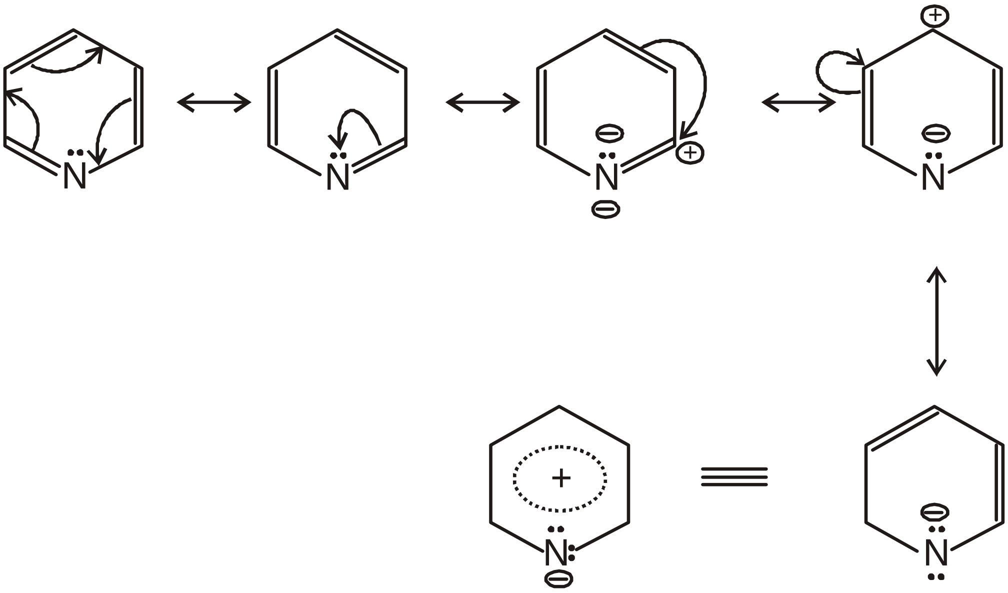
Ans :

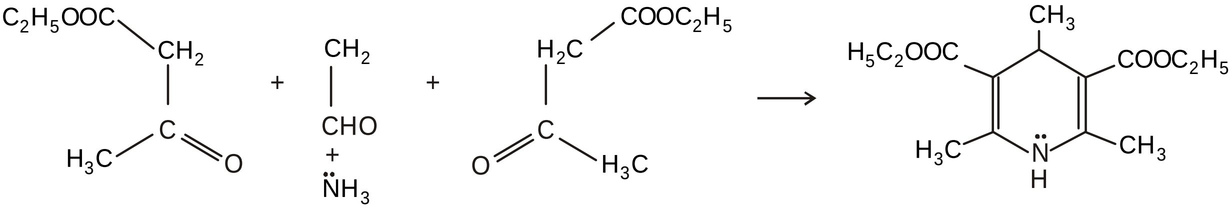
In pyridine there are five carbon atoms and one nitrogen atom which are all sp^2 hybridised Nitrogen uses its sp^2 hybrid orbitals in making two N-C bonds and the third hybrid orbital carries a lone pair of electrons. The P-orbital of Nitrogen carries a single electron similarly the p-orbital of each carbon carries a single $\bar{e}$. The P - orbital of Nitrogen lies in the same plane as the p-orbital 5 carbons. The six p-orbitals (one of nitrogen and five of carbon) overlap with each other resulting in the delocalisation of sir $\pi\bar{e}$'s in the cyclic ring system.

The lone pair of $\bar{e}$'s on nitrogen doesnot participate in delocalisation because they are perpendicular to the plane of p-orbitals of carbon.



Pyridine is a resonance hybrid of the following two Kekule's structure and other three polar structures which can be written by delocalisation of $\pi\bar{e}$'s





Q40. Why is Pyridine more aromatic than pyrrole

Ans :

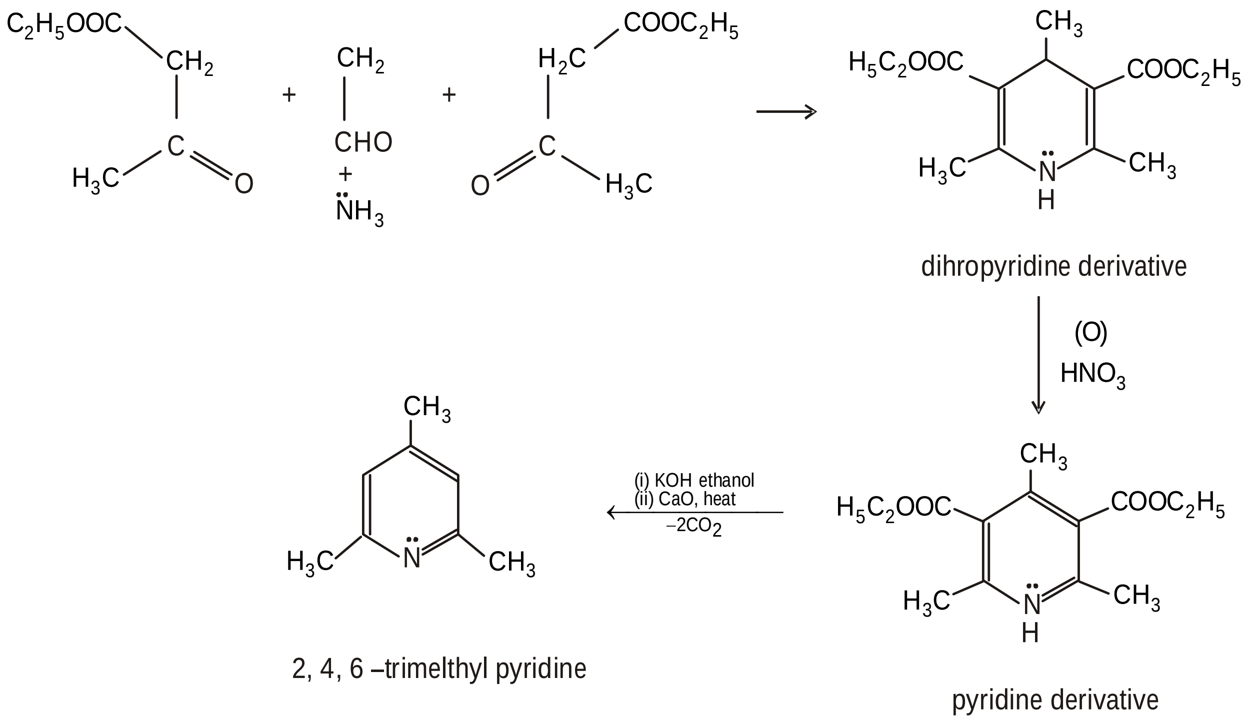
Both pyridine and pyrrole contain a nitrogen atom with one lone pair of electrons. In pyrole the lone pair of $\bar{e}$'s are included in π system but The lone pair of electrons in pyridine are not include in the π system/delocalisation which is responsible for more aromatic character.

Q41. Write the Preparation methods of pyridine

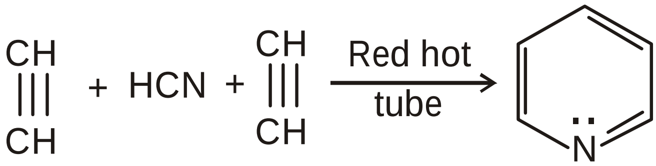
Ans :

(i) By Hantzsch method :

It involves the condensation of 2 moles of β - dicarbonyl compounds /β keto esters with aldehydes and ammonia.



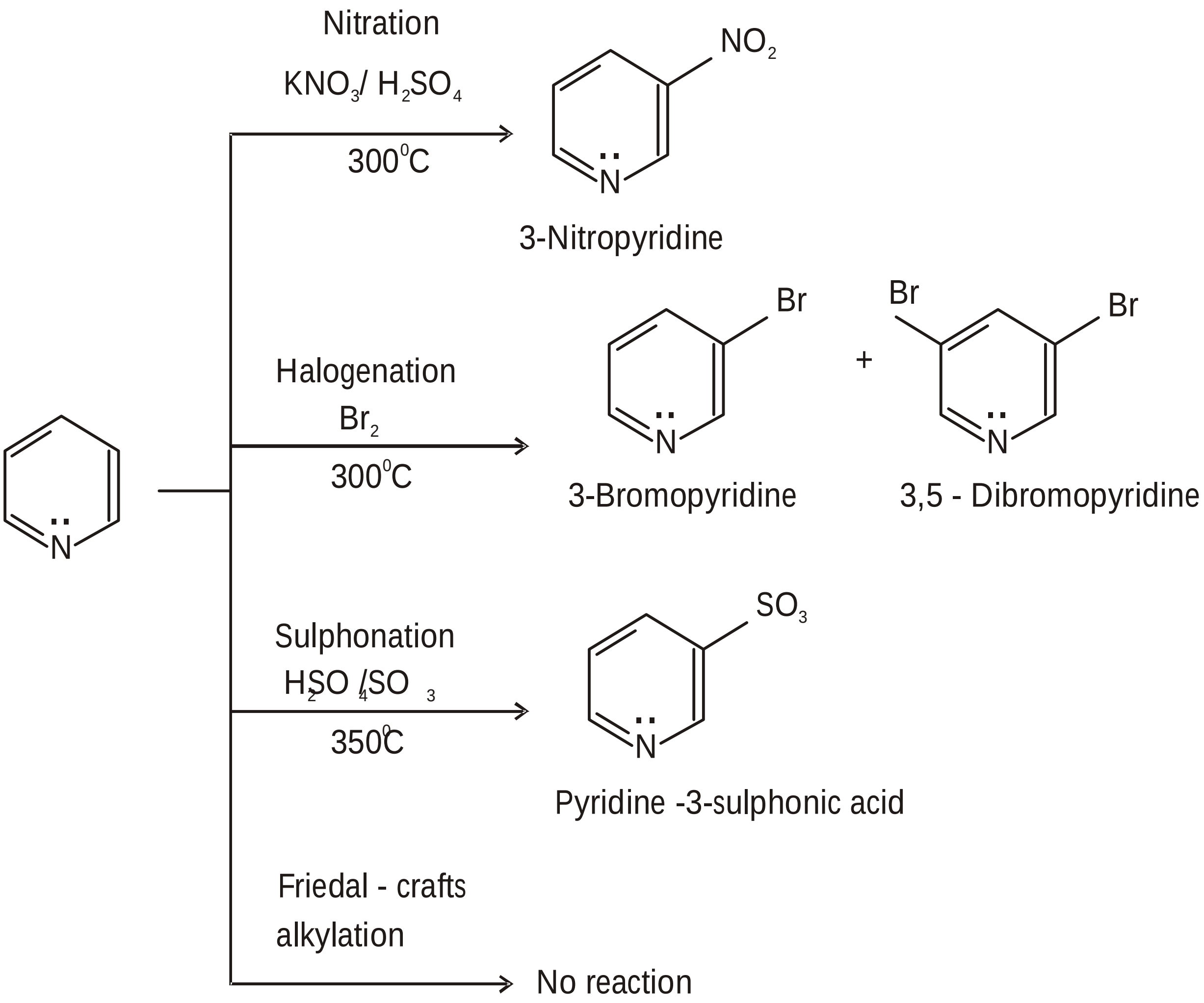
(ii) From Acetylene : Pyridine is prepared by passing a mixture of acetylene and hydrogen cyanide through a red hot tube.



Q42. Explain the electrophilic substitution reaction in pyridine.

Ans :

Pyridine undergoes, electrophilic aromatic substitution reactions like nitration, sulphonation and halogenation but under vigorous conditions. It doesnot undergo friedal crafts reaction at all. Electrophilic substitution occurs mainly at -3 or (β) position.

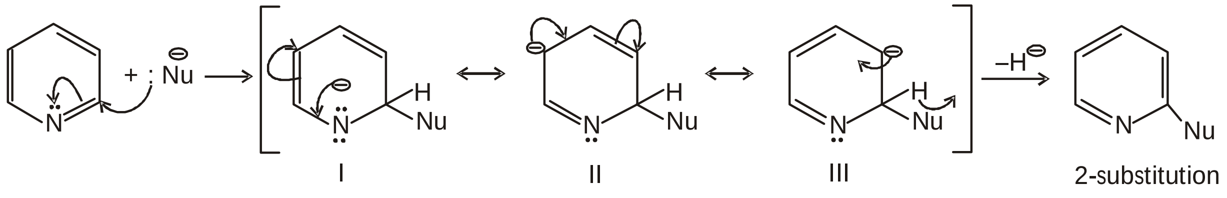


Q43. Explain the Nucleophilic substitution reaction in pyridine.

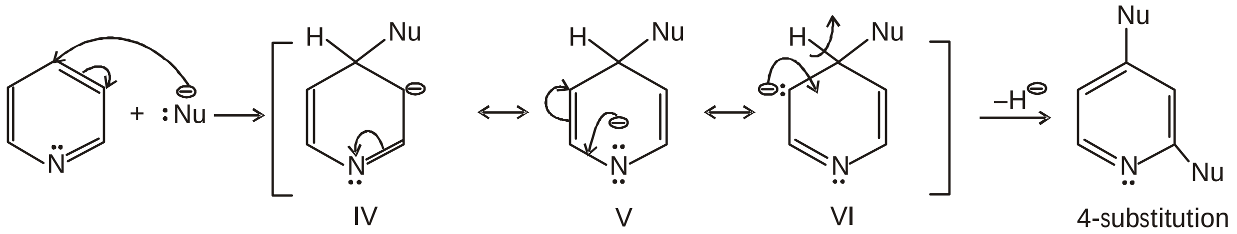
Ans :

Pyridine undergoes Nucleophilic substitution preferentially at 2 & 4 position (i.e. α and γ positions) because the intermediate anion resulting by nucleophilic attack at 2 and 4 positions are stabilised by structures I to VI.

2 (or) α - substitution

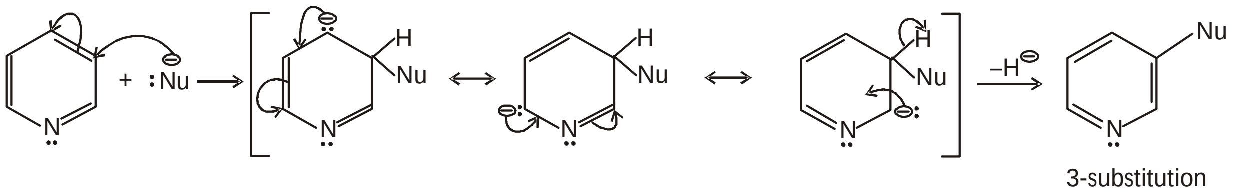


4 (or) γ - substitution



In contrast, the attack of nucleophile at 3-position will result in the formation of less stable carbonion than than that formed by 2-and 4-substitution.

3 - substitution (or) β - substitution



Q44. Why thiophene is more aromatic than furan and pyrrole explain?

Ans :

In thiophene, in sulfur the dz orbitals are available which are not present in nitrogen (pyrrols) and oxygen (furan) sulfur is less electronegative compared to nitrogen and oxygen. Due to less electronegativity the $\bar{e}$ s on sulfur participate readily in delocalisation and in the process orbitals are also utilised. As a result the number of contributing structures in thiophene are much more compared to furan and thiophene.

The high aromaticity of thiophene is from its high resonance energy 29 k.cal mol. the resonance energies for pyrrole and furan are 22.0 k.cal mol. ad 16.00 k.cal.

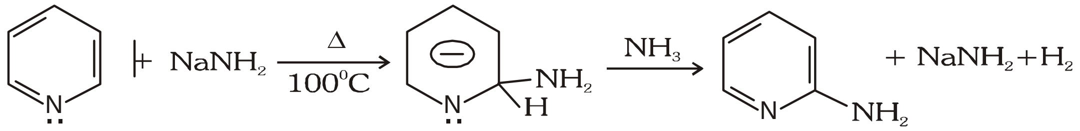
Benzene	>	Thiophene	>	Pyrrole	>	Furan
(36 k.cal)		(29 k.cal)		(22.0 k.cal)		(16.0 k.cal)

Q45. Write about chi-chibabin reaction.

Ans :

Chi-chibabin reaction :

Pyridine on heated with sodamide ($NaNH_2$) results in the formation of 2-Amino pyridine and the reaction is known as chi - chibabin reaction.



Short Question and Answers

1. What are Sugars and Non-Sugars?

Ans :

Sugars

Sugars are sweet, crystalline substances and soluble in water. They are sub divided into two groups monosaccharides the monosaccharides are polyhydroxy - aldehydes or ketones which cannot be hydrolysed further to simpler sugars.

Non-Sugars

They are usually tasteless, amorphous solids and are either insoluble in water or form colloidal suspension. Chemically polysaccharides are polymers of monosaccharides. Ex: Cellulose, Inulin.

2. Write the Tollen's Test and Fehling's Test reactions in glucose.

Ans :

Tollen's Test: Glucose reduces tollens reagent on heating to form a silver mirror.

$$HOH_2C - (CHOH)_4CHO + \underset{\text{Tollen's reagent}}{Ag_2O} \longrightarrow HOH_2C - \underset{\text{Gluconicacid}}{(CHOH)_4} - COOH + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

$$AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3 \qquad 2AgOH \longrightarrow Ag_2O + H_2O$$

Fehling's Test: Glucose reduces fehling solution on heating to form a red precipitate of cuprous oxide.

$$HOH_2C - (CHOH)_4CHO + \underset{\text{Fehling}}{2CuO} \longrightarrow HOH_2C - \underset{\text{Gluconicacid}}{(CHOH)_4} - COOH + \underset{\text{Red ppt:}}{Cu_2O\downarrow}$$

$$.CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4 \qquad 2Cu(OH)_2 \longrightarrow 2CuO + 2H_2O$$

3. Write the number of optically active isomers possible for the structure of glucose.

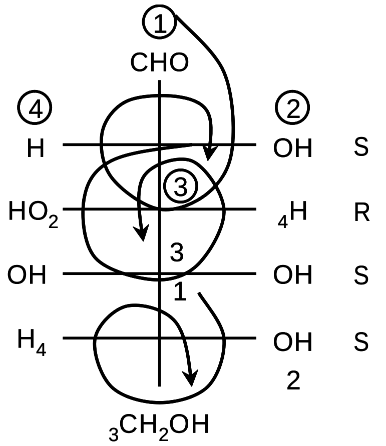
Ans :

Configuration of Glucose

Glucose possesses four asymmetric carbon atoms it can exist in $2^4 = 16$ optically active forms i.e., eight pairs of enantiomers. D and L of glucose, mannose, galactose, allose, altrose, gulose, idose, and talose.

4. Describe the configuration of glucose.

Ans :



C_2 – S configuration

C_3 – R configuration

C_4 – S configuration

C_5 – S configuration

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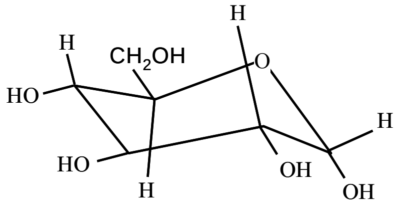
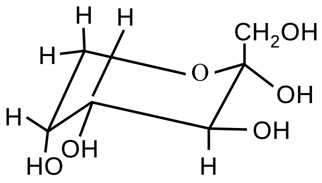
5. Write the confirmation structures for Glucose and Fructos.

Ans :



α – D(+) – Glucopynanose



α – D(–) – Fructopyranose

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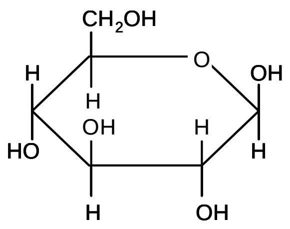
6. Write the Haworth Cyclic structures for glucose.

Ans :

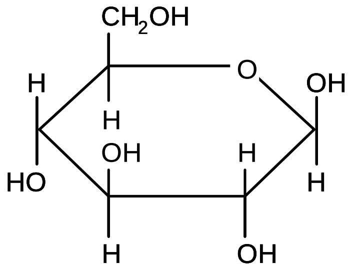
Cyclic Structure of Glucose

Five and six membered rings in the structure of sugars are denoted by the terms Furanose and Pyranose e.g.: α – D – gluco pyranose.

According to Haworth these formulae, may be written as more or less regular pentagons and hexagons.



Haworth Structure of glucopyranose (cis form)

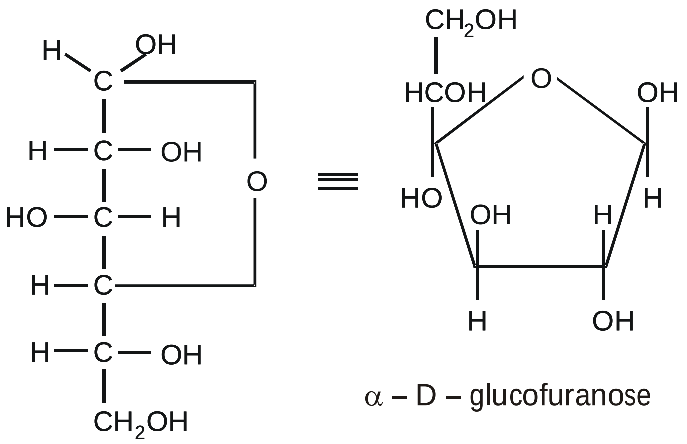


β – D – glucopyranose (Trans form)

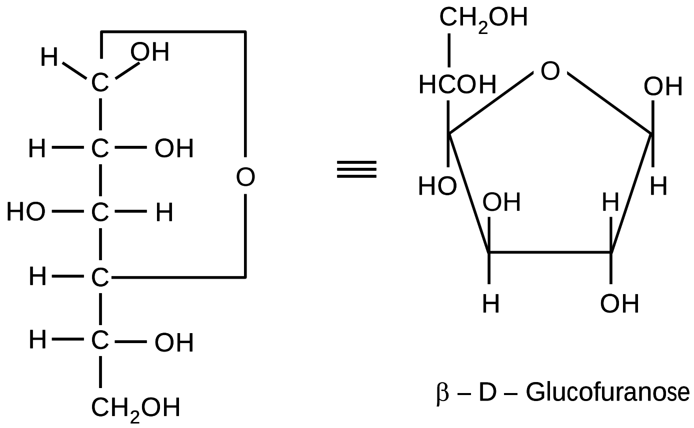
7. Write the Haworth and Fischer structures for Fructose.

Ans :

Haworth and Fischer structures for Fructose



α – D – glucofuranose

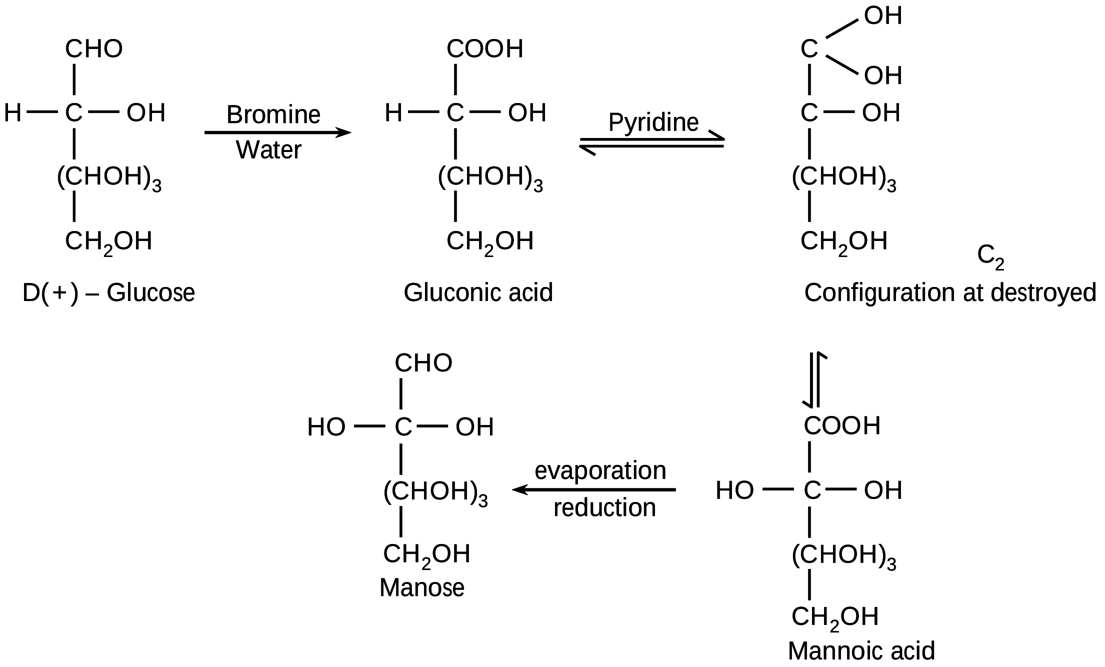


β – D – Glucofuranose

8. What are epimers.

Ans :

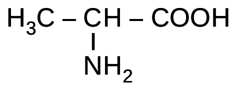
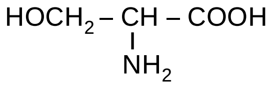
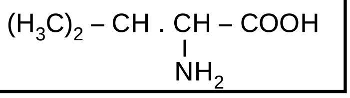
Compounds which differ only in the configuration at C_2 are called as epimers.



9. Write the Neutral Amino Acids with examples.

Ans :

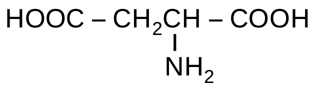
Neutral Amino Acids : These contain one amino and one carboxyl groups.

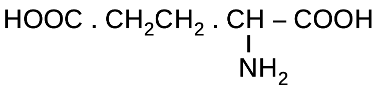
Name	Abbreviation	Group Formula
Glycine	Gly	$H_2N - CH_2 - COOH$
Alanine	Ala	 $H_3C - \underset{\underset{NH_2}{\mid}}{CH} - COOH$
Serine	Ser	 $HOCH_2 - \underset{\underset{NH_2}{\mid}}{CH} - COOH$
Valine	Val	 $(H_3C)_2 - CH\,.\,\underset{\underset{NH_2}{\mid}}{CH} - COOH$

10. Write the Acidic Amino Acids with examples.

Ans :

Acidic Amino Acids : These contain one amino and two carboxyl groups.

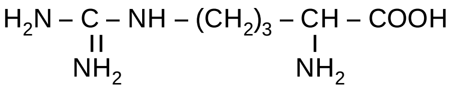
Name	Abbreviation	Formula
Aspartic acid	Asp	 $HOOC - CH_2\underset{\underset{NH_2}{\mid}}{CH} - COOH$

Glutanic acid	Glu	 $HOOC\ .\ CH_2CH_2\ .\ \underset{NH_2}{\underset{\mid}{CH}}-COOH$

11. Write the Basic Amino Acids with examples.

Ans :

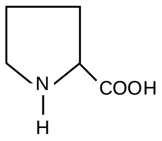
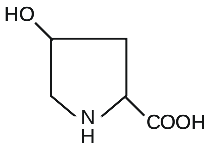
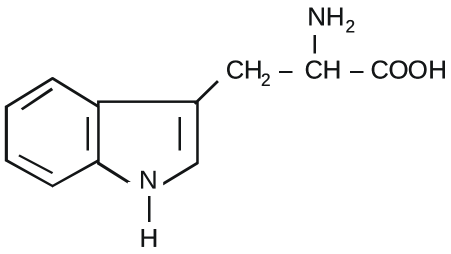
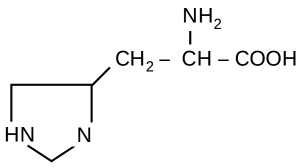
Basic Amino Acids : These contain two amino and one carboxyl groups.

Name	Abbreviation	Formula
Lysine	Lys	$H_2N(CH_2)_4\ .\ CH(NH_2)\ .\ COOH$
Arginine	Arg	 $H_2N-\underset{NH_2}{\underset{\|}{C}}-NH-(CH_2)_3-\underset{NH_2}{\underset{\mid}{CH}}-COOH$

12. Write the Heterocyclic Amino Acids with examples.

Ans :

Heterocyclic Amino Acids

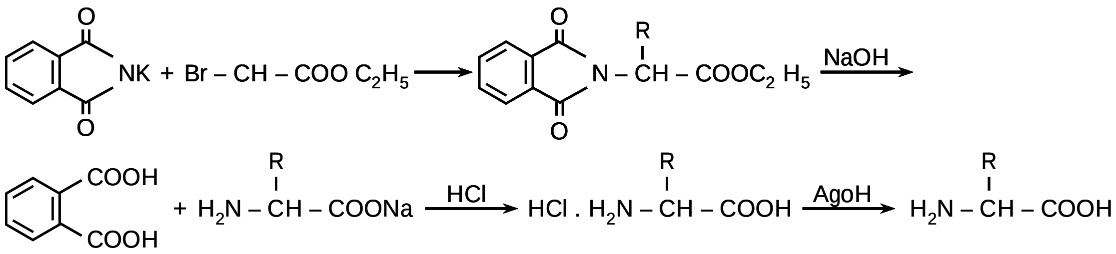
Name	Abbreviation	Formula
Proline	Pro	
Hydroxyproline	Hypro	
Tryptophan	Try	
Histidine	His	

13. Write the Garbriel Phthalimide Synthesis reactions.

Ans :

Garbriel Phthalimide Synthesis

An α – halogenated acid - ester is treated with potassium phthalimide to form a substituted phthalimide which on hydrolysis gives phthalic acid and an aminoacid.



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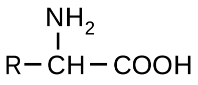
14. What is zwitter ion?

Ans :

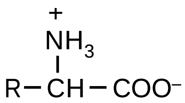
Zwitter Ion

Due to the presence of an acidic and basic are neutral and exist as dipolar or zwitter ions or inner salts in which proton from the carboxyl group has been transferred to the amino group a dipolar ion containing both a positive and a negative charge is formed.



$$R-\overset{\overset{NH_2}{|}}{CH}-COOH$$

Aminoacid



$$R-\overset{\overset{\overset{+}{NH_3}}{|}}{CH}-COO^-$$

Zwitter ion

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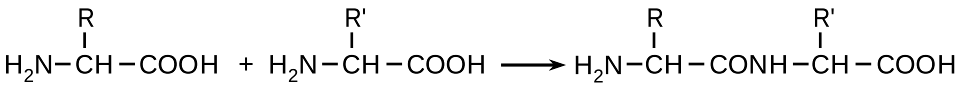
15. What is peptide bond.

Ans :

Peptide

Peptide as a substance derived from two (or) more amino acids and united through peptide bonds.



$$H_2N-\overset{\overset{R}{|}}{CH}-COOH + H_2N-\overset{\overset{R'}{|}}{CH}-COOH \longrightarrow H_2N-\overset{\overset{R}{|}}{CH}-CONH-\overset{\overset{R'}{|}}{CH}-COOH$$

---

16. Define heterocyclic campounds with examples.

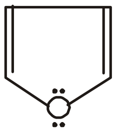
Ans :

The cyclic organic compounds in which one (or) more carbon atoms organic of the ring have been placed by other atoms such as Nitrogen, Oxygen, Sulfer are called heterocyclic compounds.

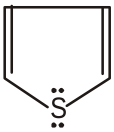
1. Five Membered Heterocyclic

These contain five atoms in the ring including the heteroatom(N,O,S)

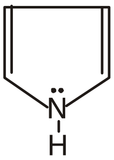
Examples :



Furan



Thiophene

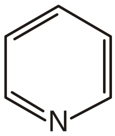


Pyrrole

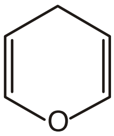
2. Six Membered Heterocyclic

These contain six atoms in the ring including the heteroatom (N, O, S)

Examples :



Pyridine



Pyran

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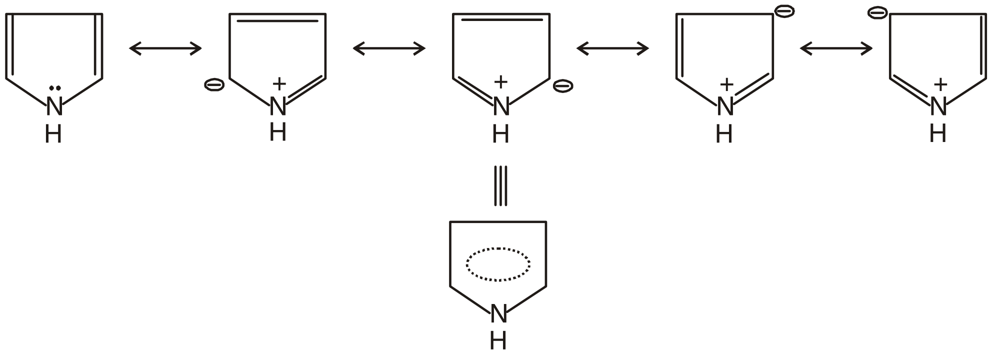
17. Write the Resonance structures of Pyrrole

Ans :



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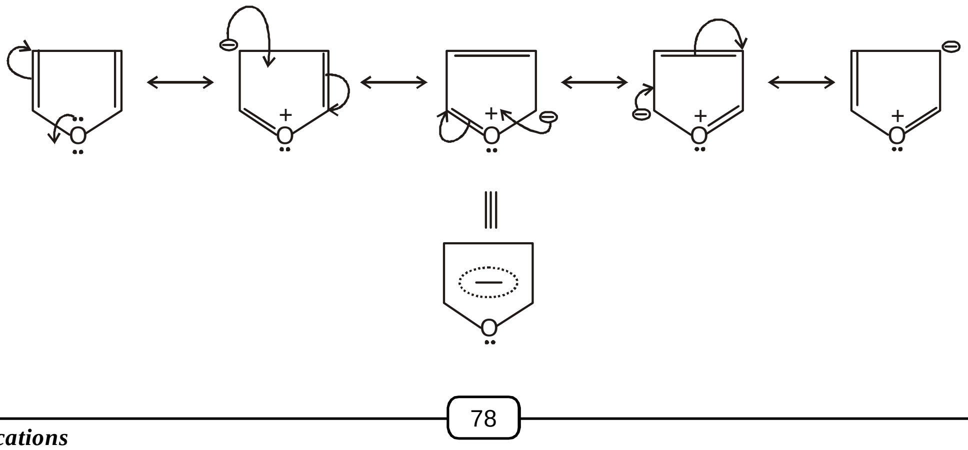
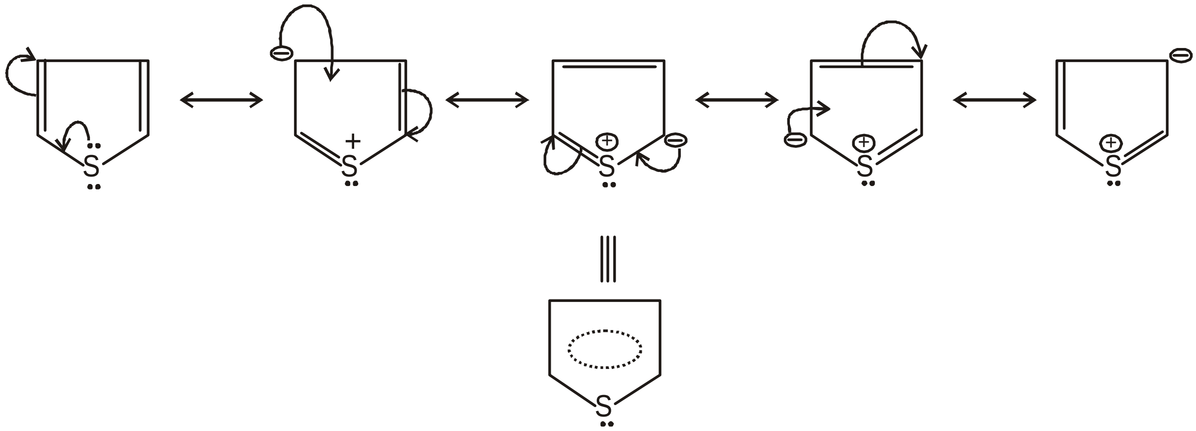
18. Write the resonance structures of furan.

Ans :



19. Write the Resonancre structures of Thiophene

Ans :

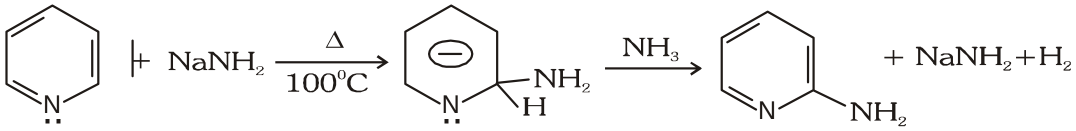


20. Write about chi-chibabin reaction.

Ans :

Chi-chibabin reaction :

Pyridine on heated with sodamide ($NaNH_2$) results in the formation of 2-Amino pyridine and the reaction is known as chi - chibabin reaction.



Choose the Correct Answers

1. Which is a disaccharide? [b]
   (a) Glucose (b) Maltose
   (c) Fructose (d) Cellulose
2. The principal sugar in blood is [b]
   (a) Fructose (b) Glucose
   (c) Sucrose (d) Galactose
3. Monosaccharides are classified according to [d]
   (a) The number of carbon atoms in the molecule
   (b) Whether they contain an aldehyde or a ketone group
   (c) Their configurational relationship to glyceraldehyde
   (d) All the above
4. α-D-Glucose is different from b-D-Glucose [a]
   (a) In the configuration at C - 1
   (b) Because they are mirror images of each other
   (c) Because they are enantioners
   (d) Because they are geometrical isomers
5. Mutarototation is a term related to [a]
   (a) Interconversion of anomers
   (b) Relationship of D and L-configuration
   (c) Hydrolysis of sucrose
   (d) Number of monosaccharides in a carbohydrate
6. The reagent that can be used to differentiate an aldose and aketoseis is [b]
   (a) Bromine water (b) Fehling’s solution
   (c) Tollens reagent (d) none of the above
7. A reducing sugar will [a]
   (a) React with fehlings test (b) Not react with Fehling’s test
   (c) Always be a ketone (d) None of the above
8. The monosaccharide obtained by hydrolysis of starch is [a]
   (a) D-Glucose (b) Maltose
   (b) L-Glucose (d) Ribose
9. Which of the following is a polysaccharide? [d]
   (a) Glucose (b) Ribose
   (c) Sucrose (d) Cellulose

10. Which class of compounds is referred to as aldoses [a]

    (a) Polyhydroxy aldehyde

    (b) Compounds containing both aldehyde and ketonic carbonyl groups

    (c) Polycyclic aldehydes

    (d) Polyhydroxy ketones

11. The pH at which the aminoacid shows no tendency to migrate when placed in an electricfield is known as [a]

    (a) Isoelectric point (b) Dipolemoment

    (c) Iodine number (d) Wave length

12. A Zwitterion has which of the following properties [d]

    (a) No net charge (b) A high melting point

    (c) Soluble in water (d) All of these

13. Which of the following is the main structural feature of proteins? [a]

    (a) Peptide linkage (b) Ester linkage

    (c) Ether linkage (d) α, β-linkage

14. Glycine is a unique aminoacid because it [a]

    (a) Has no chiral carbon (b) Has a sulfar containg R group

    (c) Cannot form a peptide bond (d) Is an essential aminoacid

15. Proteins are [a]

    (a) Polyamides (b) Polymers of ether

    (c) α- aminocarboxylic acids (d) Polymers of propylene

16. The α-Helix is a common form of [a]

    (a) Primary structure (b) Tertiary structure

    (c) Secondary structure (d) None of the these

17. On hydrdysis of proteins give [a]

    (a) Amino acids (b) Hydrous acids

    (c) Fatty acids (d) Alcohol

18. Which of the following reactions is suitable for the prepn amino acids [b]

    (a) Schmidt reaction (b) Hofmann's degradation

    (b) Strecker's synthesis (d) Reduction of nitrocompounds

19. Which of the following tests is not used for testing proteins [b]

    (a) Ninhydrin test (b) Biuret test

    (c) Xanthoproteic test (d) Tollen's test

20. The five elements present in most naturally occurring proteins are [a]

    (a) C, H, O, P and S (b) N, C, H, O & I

    (c) N, Z, C, H, O (d) C, H, O, S and I

21. How many types of carbon atoms are present in pyrrole? [a]
(a) 1 (b) 2
(c) 3 (d) 4

22. Which of the following is a six membered heterocyclic? [a]
(a) Furan (b) Pyrrole
(c) Thiophene (d) Pyridine

23. Which of the following is not aromatic? [c]
(a) Pyrrole (b) Pyridine
(c) Pyran (d) Furan

24. Which of the following can undergo Diel's Alder reaction? [a]
(a) Furan (b) Pyrrole
(c) Thiophene (d) All the three

25. Coupling reaction is shown by [d]
(a) Pyrrole (b) Furan
(c) Thiophene (d) All the above three

26. Pyrrole does not undergo [d]
(a) Halogenation (b) Sulphonation
(c) Nitration (d) Friedel-Crafts reaction

27. Pyrrole is aromatic because it has [c]
(a) Five membered ring (b) Conjugated double bonds
(c) Aromatic sexet (d) All the above

28. Which of the following statements is incorrect? [c]
(a) Pyrrole resembles phenol
(b) Thiophene is more reactive than benzene
(c) Pyrrole, furan and thiophene are easily hydrogenated to their corresponding tetrahydro product
(d) Electrophilic substitution of 2-substituted pyrrole mainly takes place at position 5

29. The most reactive five membered heterocyclic is [a]
(a) Furan (b) Pyrrole
(c) Thiophene (d) All the above

30. Pyrrole is : [a]
(a) Acidic (b) Basic
(c) Amphoteric (d) All the above

31. The heterocyclic with the highest resonance energy is [a]
(a) Thiophene (b) Furan
(c) Pyrrole (d) All the above

Fill in the blanks

1. Which reagent converts sugars to osazones ________.
2. In solution fructose exsists as a ________, ________.
3. D-Glucose / L-glucose are ________.
4. Positive tollen's test indicates ________.
5. Example for polysaccharide is ________.
6. The composition of honey a mixture of ________.
7. In the chain - lengtheing killiani - fischer synthesis the source of the new carbon atom in ________.
8. The monosaccharide obtained by hydrolysis of starch is ________.
9. Starch is a mixture of ________.
10. The number of asymmetric carbon atoms in the α-D-Glucopyranose molecule is ________.
11. Which organic functional group forms the peptide bond of bonds ________.
12. ________ usually maintain the secondary structure of protein.
13. ________ maintains the primary structure of a proteins.
14. Zwitter ion is ________.
15. The double helical structure of DNA is held together by ________.
16. Structure of Glycine is ________.
17. Digestion of proteins involves ________.
18. Precipitation or coagulation of proteins may be caused by ________.
19. When Glycine is heated it forms ________.
20. Irreversible precipitation of proteins caused by heating is called ________.
21. The order of resonance energy in five membered Heterocyclic compounds ________.
22. Electrophilic substitution is favourable in pyrrole and furan at which position ________.
23. The armoatic character of pyrrole is due to the presence of ________.

ANSWERS

1. C_6H_5- NH - NH_2 Phenylhydrazine
2. Consisting of two furanose ring , Single furanose ring
3. Enantiomers
4. A carbohydrate can exist as an open chain aldose or ketose
5. Cellulose
6. Glucose & fructose
7. HCN
8. D-Glucose
9. Amylose + amylopection
10. 5
11. Amide
12. Hydrogen bonds
13. Covalent bodns
14. A compound that can ionize both as a base and an acid
15. Hydrogen bond
16. $H_2N – CH_2 – COOH$
17. Cleavage of peptide linkages
18. Heat
19. Diketopiperazine
20. Denaturation
21. Thiophene > phyrrole Furan
22. 2^{nd} I 5^{th}
23. Aromatic sextel.

One Mark Answers

1. **Name one reducing and one non reducing disaccharide. Which polysaccharide is stored in the liver of animals?**

Ans :

Maltose and lactose are reducing while sucrose is non reducing sugar. Glycogen is stored in the liver of animals.

2. **Sucrose is a non-reducing sugar while both glucose and fructose are reducing in nature. Explain.**

Ans :

The reducing nature of both glucose and fructose is due to the presence of carbonyl group (Aldehydes and ketones). Since these groups are not free in sucrose, therefore it does not show the test of carbonyl group it is thus non reducing sugar.

3. **Althrough glucose and fructose differ in their structures they form the same orazone. comment.**

Ans :

Glucose and fructose differ in their structures at C_1 and C_2 while the structures of the remaining four carbon atoms are the same. As only the first two carbon atoms are involved in the formation of osazone with pherylhydrazine both glucose and fructose form the same osazone.

4. **Fructose has no aldehyde group but acts as a reducing agent. Explain.**

Ans :

Fructose contains a ketonic group but still it reduces Tollen's reagent the reason is that fructose undergoes Lobry de Bruyn Ekenstein rearrangement in the alkaline medium and given a mixture of glucose, fructose and mannose. The reducing reactions are due to the formation of glucose and mannose which contain aldehydic group.

5. **Two molecules of glycine when condence form a simple peptide. Name the peptide.**

Ans :

Glycyl glycine.

6. Write few sources of proteins.

Ans :

Proteins are found in soya bean, skimmed milk (powder) powder milk (whole), fish, mutton etc.

7. Pyrrole, furan and thiophene are less aromatic or more reactive than benzene, hence their order of reactivity can be written as,

Ans :

Pyrrole > Furan > Thiophen > Benzene.

8. Name the reaction given by furan and not by pyrrole and thiophene.

Ans :

Diel's Alder reaction.

UNIT - III

(Physical Chemistry)

S4-P-1: Chemical Kinetics

Introduction to chemical kinetics, rate of reaction, variation of concentration with time, rate laws and rate constant. Specific reaction rate. Factors influencing reaction rates: effect of concentration of reactants, effect of temperature, effect of pressure, effect of reaction medium, effect of radiation, effect of catalyst with simple examples. Order of a reaction. First order reaction, derivation of equation for rate constant. Characteristics of first order reaction. Units for rate constant. Half- life period, graph of first order reaction, Examples-Decomposition of H_2O_2 and decomposition of oxalic acid, Problems. Pseudo first order reaction, Hydrolysis of methyl acetate, inversion of cane sugar, problems. Second order reaction, derivation of expression for second order rate constant, examples Saponification of ester, $2O_3 \rightarrow 3O_2$, $C_2H_4 + H_2 \rightarrow C_2H_6$. Characteristics of second order reaction, units for rate constants, half- life period and second order plots. Problems

S4-P-2: Photochemistry

Introduction to photochemical reactions, Difference between thermal and photochemical reactions, Laws of photo chemistry- Grotthus Draper law, Stark–Einstein's Law of photochemical equivalence. Quantum yield. Examples of photo chemical reactions with different quantum yields. Photo chemical combinations of H_2–$Cl_2$and H_2–Br_2 reactions, reasons for the high and low quantum yield. Problems based on quantum efficiency. Consequences of light absorption. Singlet and triplet states. Jablonski diagram. Explanation of internal conversion, inter-system crossing, phosphorescence, fluorescence.

S4-P-1: CHEMICAL KINETICS

Q1. What do you understand by the term chemical kinetics.

Ans :

The measurements of rates of reactions proceeding under given conditions of temperature, pressure and concentration is dealt under the heading of chemical kinetics.

Q2. Define rate of a reaction? What are its units?

Ans :

Rate of Reaction

Rate of reaction as the decrease of concentration of the reactant(s) or increase in concentration of the product(s) per unit time. Mathematically, the rate of reaction can be expressed as below:

$$\text{Rate of reaction} = \frac{\text{Amount of reactant consumed}}{\text{Time interval}}$$

or $$\text{Rate of reaction} = \frac{\text{Amount of product produced}}{\text{Time interval}}$$

Now let us consider a simple hypothetical reaction of the type

$$A \rightarrow X$$

The concentration of a substance, (e.g., A) at a given time t is denoted either by C_A or [A]. Finite changes in time and concentration are represented by Δt and ΔC_A and changes of infinitely small order are denoted by dt and dC_A respectively.

$$\text{Rate of reaction (r)} = \frac{dx}{dt}$$

Concentration of the reactant decreases with time, the term dx used for reactant becomes negative and hence the right hand side term in the above equation bears a negative sign. Thus the rate of reaction is given by the negative sign and hence the above equation becomes.

$$r = -\frac{d[A]}{dt}$$

Q3. Define order of reaction.

Ans :

The order of reaction can be defined as the sum of the power of the concentration terms.

Although most of the reactions have a whole number order, certain reactions having fractional orders (e.g., 1/2, 3/2, etc.) are also known. For example, the order of reaction of the ortho-para hydrogen conversion is 3/2 since its rate is expressed as below:

$$\frac{dx}{dt} = k[H_2]^{3/2}$$

Similarly, the order of dissociation of acetaldehyde in the gas phase is 3/2.

$$\frac{dx}{dt} = k[CH_3CHO]^{3/2}$$

Q4. Define specific reaction rate.

Ans :

Consider the following reaction:

$$A \rightarrow X$$

Rate of reaction,

$$r = -\frac{dx}{dt} = -\frac{d[A]}{dt} = k[A]$$

where [A] represents the concentration of the reactant A and k is the proportionality constant, called the velocity constant, rate constant or specific reaction rate at the given temperature. It may be defined as the fraction of A that reacts per unit time. If concentration of A is unity, i.e., [A] = 1, then

$$r = k$$

Thus at a given temperature and when the concentration of the reactant is unity the rate constant of a reaction involving a single reactant is equal to the rate of the reaction.

Now let us consider reaction involving two reaction, *viz*. A and B.

$$A + B \rightarrow \text{Products}$$

then $$r = \frac{dx}{dt} = k\,[A][B]$$

where [A] and [B] are the concentrations of the reactants A and B at a given time. Now again if concentration of both the reactants is unity, i.e.,

$[A] = [B] = 1$, Then

$$r = k$$

In general, the rate constant of a reaction is equal to the rate of the reaction, when the concentration of each of the reactants is unity.

$$nA + xB \rightarrow \text{Products}$$

the rate of reaction will be given by the following expression :

$$\frac{dx}{dt} = k[A]^n \times [B]^x$$

The law states that the rate of chemical reaction is proportional to the concentration of the reacting species raised to the power of their coefficients in chemical equation.

Q5. Explain the factors effecting on the rate of reactions.

Ans : **(Imp.)**

There are several factors which influence the rate of reaction, only the important ones are described below:

1. Concentration of Reactants

The rate of a reaction is proportional to the concentration of the reacting substance(s) (reaction rate law). The rate of reaction decreases with the increase in time since, as the reaction progresses, i.e., with the increase in time the concentration of the reactant(s) decreases.

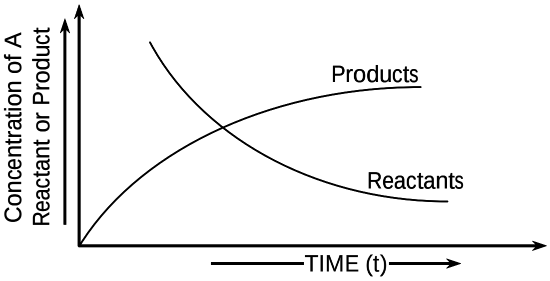


Fig.: Change of concentration of reactants and products with time in a chemical reaction

2. Effect of Temperature

The rate of chemical reaction increases as the temperature is raised. Consequently, reactions are carried out at elevated temperatures so that a good yield of the products can be obtained in a reasonable time.

3. Effect of Catalyst

Generally a catalyst increases the rate of a reaction at a given temperature. Further a catalyst is generally specific in its actions, i.e., it may effect the rate of one particular reaction only. For exmaple, manganese dioxide can catalyse only the decomposition of potassium chlorate to give oxygen.

4. Effect of the nature of reactants and products

Rates of reactions are considerably influenced by the nature of reactants and products. Reactions involving greater number of breaking and formation of bonds are slow at room temperature that those which involve lesser number of bond cleavage and formation. Consider the following two reactions:

(i) $2NO + O_2 \longrightarrow 2NO_2$

(ii) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

The reaction (i) involves breaking of one bond in NO and formation of two new bonds in NO_2 while the reaction (ii) involves breaking of four bonds in methane and formation of two bonds in CO_2 and four bonds in water, the reaction (i) is much faster thant the (ii) at the same temperature.

5. Effect of surface area of reactants

The factor has significance only in case of heterogeneous reactions. Larger surface area of solid reactants and catalysts tend to increase the rate of a reaction. The surface are for the same mass increases with the decrease in particle size, the smaller particles will react more rapidly than the lareger partilces.

6. Effect of radiation

The rate of certain reactions increases by absorption of photons of certain radiations. Such reactions are known as photochemical ractions.

Q6. Derive an expression for the rate constant of a first order reaction. Give two examples for first order reaction.

Ans : **(Imp.)**

First Order Reactions

Those reactions whose rate is determined by the change of only one concentration term are known as first order reactions. Such reactions can be represented by the following general types:

Ex : (1) $H_2O_2\ aq \rightarrow H_2O + \frac{1}{2}O_2(g)$ (2) $NH_4NO_2 \rightarrow 2H_2O + N_2(g)$

$$A \rightarrow \text{Products}$$

$$A + B\ (\text{excess}) \rightarrow \text{Products}$$

In both the cases the reaction rate is given by

$$\text{Rate} = \frac{dx}{dt} = \frac{-d[A]}{dt} = k[A]$$

i.e., $$-\frac{d[A]}{dt} = k[A]$$

The above relation shows infinitely small change of concentration in infinitely small interval of time which is very difficult to estimate, this relation as such is of little help in determining the value of rate constant k. However, the value of rate constant can be determined by using integral calculus as the new expression will involve measurable change in concentration of the reactant in measurable intervals of time.

Let the initial concentration of A be C_0, and the concentration after a time t seconds be C. Substituting the value of concentration in eq. (v), we get.

$$-\frac{dC}{dt} = kC$$

or $$-\frac{dC}{dt} = k\,dt$$

On integrating

$$-\int_{C_0}^{C}\frac{dC}{C} = k\int_0^t dt$$

$$kt = -\ln C + \text{constant of integration}$$

Now at the beginning of the reaction (i.e., when t = 0), $C = C_0$, so

$$0 = -\ln C_0 + \text{constant}$$

$$\text{Constant} = \ln C_0$$

Substituting this value for the constant of integration

$$kt = \ln C_0 - \ln C$$

$$= \ln\frac{C_0}{C} = 2.303\log\frac{C_0}{C}$$

or $$k = \frac{2.303}{t}\log\frac{C_0}{C} \qquad \text{...(vi)}$$

This is the equation for first order reaction; where C_0 is the concentration of the reactant at start, i.e., when t = 0 C is the concentration of the reactant after time t. The constant k of this equation is called the first order rate constant.

The initial concentration of the reactant (i.e., when t = 0) is a moles per unit volume and after the time t seconds the concentration reduces to (a – x) moles per unit volume of the reactant, i.e., x moles of the reactant have reacted. In short, when C_0 = a and C = (a – x), the Equation (vi) takes the shape of Eq. (vi a).

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

Characteristics of First Order Reactions

1. Units of First Order Rate Constant

The fraction C_0/C is a ratio of two concentrations, the value of velocity constant is independent of the actual concentration units used. The velocity constant, therefore, has the units of 1/time, and is usually expressed in second^{-1}.

$$k = \frac{2.303}{\text{time}} \log \frac{\text{moles / litre}}{\text{moles / litre}}$$

$$k = \text{time}^{-1}$$

Thus if time is expressed in seconds, k = second^{-1}.

2. Half-life Period of a First Order Reaction ($t_{1/2}$)

The equation (vi) can also be used to calculate the time taken for any given proportion of the reactant to disappear. In general, half-life period of a reaction is the time required to convent the concentration ($C_0/2$). Thus by substituting the value $C_0/2$ in place of C in equation (vi), the half-life of the reaction can be ascertained.

$$t_{1/2} = \frac{2.303}{k} \log \frac{C_0}{C_0 / 2}$$

$$= \frac{2.303}{k} \log 2 \qquad (\log 2 = 0.313)$$

$$= \frac{0.693}{k}$$

3. Evaluation of k

The first order rate constant can be evaluated by two methods, *viz*., (i) by means of first order reaction Equation (vi) or vi (a) and (ii) by a graphical method.

In the graphical method log a/(a–x) is plotted against the corresponding time intervals t when a straight line passing through the origin will be obtained. The slope of this, straight line be equal to $\frac{k}{2.303}$. Thus form the slope, the value of k can be calculated.

Q7. What is meant by Half - period?

Ans :

Half-Period

Half-life period of a first order reaction is independent of the initial concentration, a characteristic of the first order reactions.

The quantity of the reactant present after two half-times will be 1/2 × $1/2C_0$, i.e., $(1/2)^2C_0$; similarly after n halftimes the quantity of the reactant left, i.e., C_n may be given by

$$C_n = [1/2]^n \times C_0$$

Q8. What are pseudo molecular reactions? Give suitable examples.

Ans :

Hydrolysis reactions in neutral or acid solution are also of first order. This is because the amount of water used greatly exceeds that required for the reaction, while the acid acts as a catalyst and is, therefore, not used up during the reaction. Some examples are cited below.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{acid}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{\text{acid}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Benzene diazonium Chloride}}{C_6H_5N_2Cl} + H_2O \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

In all the above reactions although two molecules are used, the reactions are said to be unimolecular since, the amount of water (one of the reactants) nearly remains same during the course of reactions, such reactions, Sometimes known as pseudo monomolecular or pseudo first order reactions.

The acid catalysed hydrolysis of can sugar (commonly known as inversion of cane sugar) and esters are used for comparing the relative strength of acids.

Q9. Derive an expression for the second order reaction and write the characteristics.

Ans : **(Imp.)**

Second Order Reactions

Reactions whose rate is determined by change of two concentration terms are known as second order reactions. Second order reactions may be of two types:

(i) When two molecules of the same reactant react and thus the rate is determined by the two concentration terms of the same molecule, e.g.

$$2HI \rightarrow H_2 + I_2$$

or, In general, $2A \rightarrow \text{Products}$

$$A + A \rightarrow \text{Products}$$

In such cases, the rate of the reaction, at any moment, may be given by

$$= \frac{d[A]}{dt} = k[A]^2$$

where [A] is the concentration of the reactant A at any given time t, and k is the rate constant.

(ii) When two molecules of the different reactants react and concentration of both the molecules vary during the reaction; i.e., reaction rate is determined by the change of two concentration terms of the two different reactants, e.g.,

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

or, in general $\quad A + B \rightarrow \text{Products}$

The rate of reaction of such cases may be given by

$$-\frac{d[A]}{dt} = k[A][B]$$

where [A] and [B] are the concentration of the reactants A and B respectively at any given time t and k is the velocity constant.

a) Rate Constant of Second Order Reactions Having Only One Reactant

From the above discussion we know that the reaction rate of such reactions is given by

$$-\frac{d[A]}{dt} = k[A][A]$$

$$= k\,[A]^2$$

or $$-\frac{d[A]}{[A]^2} = k\,dt$$

Now suppose C_0 is the initial concentration of the reactant at the commencement of the reaction, i.e., when t = 0 seconds and C is the concentration at time t seconds. On integrating the equation between the limits of time from 0 to t and concentration from C_0 to C, we have

$$-\int_{C_0}^{C} \frac{d[A]}{[A]^2} = \int_0^t k\,dt$$

$$\left[\frac{1}{[A]}\right]_{C_0}^{C} = k[t]_0^t$$

or $$\frac{1}{C} - \frac{1}{C_0} = k(t-0)$$

$$\frac{1}{C} - \frac{1}{C_0} = kt$$

$$k = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right)$$

This equation is known as second order rate equation and permits easy calculation of the rate constant k, known as second order rate constant.

In case the initial concentration of the reactant is a and the concentration at time t left behind when x mole of the reactant has reacted is (a – x), i.e.,

$$C_0 = a \quad \text{and} \quad C = (a - x)$$

The equation takes the shape

$$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

or

$$k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$

Evaluation of k

The second order rate constant k can be evaluated by using the rate equation (x) or (xi) for which we must know the concentration (C or a – x) of the reactant at different intervals of time t; the initial concentration C_0 or a of the reactant at commencement of the reaction being already known.

The value of k can also be determined by the graphical method in which x/a(a – x) is plotted against time t when a straight line passing through the origin will be obtained. The slope of this straight line will be equal to k.

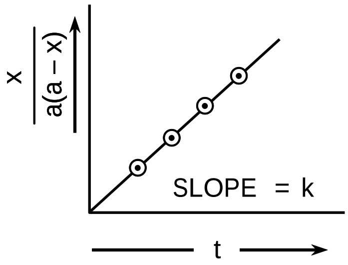


Fig.: Plot of x/a (a – x) vs t for a second order reaction

b) Rate Constant of Second Order Reactions Having Two Different Reactants

In general, the second order reaction of this type may be written as below:

$$A + B \rightarrow \text{Products}$$

In such a reaction again there are two possibilities.

(a) When both the reactants have the same initial concentration, i.e., [A] = [B]. Thus, the rate of equation may be written.

$$-\frac{d[A]}{dt} = k[A]\,[A] = k[A]^2$$

or

$$-\frac{d[B]}{dt} = k[B]\,[B] = k[B]^2$$

Since equation (xii) and (xii a) are the same as equation (viii), the kinetics of such reactants follow the similar trend as that followed by second order reactions having only one reactant.

(b) When the two reactants A and B have different initial concentrations. Let us consider reaction.

$$A + B \rightarrow \text{Products}$$

Let the concentration of A and B at t = 0 is a and b
and concentration at time t is (a – x) and (b – x)

$$-\frac{dx}{dt} = k\,(a-x)\,(b-x)$$

or
$$-\frac{dx}{(a-x)(b-x)} = k\,dt$$

On integration

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

or
$$\frac{1}{a-b}\ln\frac{a-x}{b-x} = kt + I$$

Where I is the integration constant, at t = 0 and x = 0 the value of I has been calculated.

$$I = \frac{1}{a-b}\ln\frac{a}{b}$$

Substituting the value of I in (xiii) we get

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

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

or
$$k = \frac{1}{t}\left[\frac{2.303}{a-b}\log\frac{b(a-x)}{a(b-x)}\right]$$

If one of the reactants is taken in a large excess, the reaction conforms to the first order reaction. Let us consider the rate law given by equation.

$$k = \frac{1}{t}\left[\frac{2.303}{(a-b)}\log\frac{b(a-x)}{a(b-x)}\right]$$

Suppose 'a' is in large excess so that x and b may be negligibly small in comparison to b. Under such circumstance, above equation may be written as,

$$K = \frac{1}{t}\left[\frac{2.303}{a}\log\frac{ba}{a(b-x)}\right]$$

or
$$= \frac{2.303}{ta}\log\frac{b}{(b-x)}$$

The above equation is identical with the equation (via) for the first order reaction.

Evaluation of k

The value of k can be determined with the help of equation for which concentration of the reactants A and B at any given time t, i.e., (a – x) and (b – x) are determined and since the initial concentration a and b of the two reactants are known, the value of k can easily be ascertained.

The value of k can also be evaluated graphically fro which the quantity $\frac{2.303}{a-b}\log\frac{b(a-x)}{a(b-x)}$ is plotted against time t; the slope of the line will give the value of k.

Units of Second Order Rate Constant

From the equations it is clear that the denominators contain one additional concentration terms in these equation and hence, the value of k depends on the units of both time and concentration. Dimensionally, from equation (xvi),

$$k = \frac{1}{\text{time}} \times \frac{\text{moles / litre}}{\text{moles / litre} \times \text{moles / litre}} = \text{litre moles}^{-1}\ \text{time}^{-1}$$

Similarly, according to equation (xiv)

$$k = \frac{1}{\text{time}} \times \frac{\text{moles / litre} \times \text{moles / litre}}{\text{moles / litre} \times \text{moles / litre} \times \text{moles / litre}} = \text{litre moles}^{-1}\ \text{time}^{-1}$$

Half-life Period of a Second Order Reaction

The half-life period can be evaluated from equation (xvi) by substituting

$$x = \frac{a}{2} \text{ and } t = t_{1/2}$$

$$k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$

$$k = \frac{1}{t_{1/2}}\left[\frac{a/2}{a\left(a-\frac{a}{2}\right)}\right]$$

$$t_{1/2} = \frac{1}{k}\left[\frac{a/2}{a\left(a-\frac{1}{2}\right)}\right] = \frac{1}{k}\left[\frac{a/2}{a^2/2}\right]$$

$$= \frac{1}{k}\left[\frac{1}{a}\right] = \frac{1}{ka}$$

Thus the half-life of a second order reaction is inversely proportional to the initial concentration of the reactants and k(half-life of first order reaction which is inversely proportional to only k and independent of a).

Q10. Write the derivation for the zero order reaction and give the characteristics.

Ans : **(Imp.)**

A reaction whose rate does not depend on concentration of reactants is called a zero order reaction. Obviously, for such reactions the rate of the reaction remains uniform througout i.e.,

$$\text{Rate} = \text{Constant}$$

Mathematically,

$$\frac{dx}{dt} = \text{constant}$$

$$= k$$

where *k* is the rate constant for the zero order reaction

or $dx = k \, . \, dt$

On integrating, we get

$$\int dx = \int k \, . \, dt$$

or $x = kt + \text{constant of integration (I)}$

when $t = 0, x = 0$ and hence $I = 0$

Therefore, $x = kt$

This is the zero order rate reaction according to which amount of substance reacted $\propto$ time

Characteristics of Zero Order Reactions

1. **Units of zero order rate constant, k.** According to the zero order rate equation,

$$x = kt$$

or $$k = \frac{x}{t} = \frac{\text{moles / litre}}{\text{time}}$$

$$= \text{mole litre}^{-1} \text{ time}^{-1}$$

Since concentration term is involved in the unit of k, the numerical value of the rate constant k depends on the unit in which concentration is expressed.

2. **Half-life (fractional) period of a zero order reaction :** The expression for the half-life period (i.e., time taken for converting the original concentration of the reactants to one half) may be obtained as follows:

When $x = \frac{a}{2}, t = t_{1/2}$

where "a" is the initial amount, i.e., when $t = 0$, and x is the amount reacted at time t which is $t_{1/2}$ in case of half-life period.

Substituting the value of x and t in the zero order reaction,

$$x = kt$$

$$\frac{a}{2} = k \times t\tfrac{1}{2}$$

$$t_{1/2} = \frac{a}{2k}$$

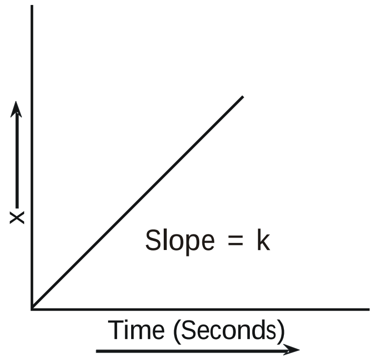


Fig.: Plot of x vs t for a zero order reaction

3. **Evaluation of k :** A plot of x against t will yield a straight line passing through the origin. The slope of this straight line is k.

Examples of Zero order Reactions

Two types of reactions have been found to be of zero order.

(i) Photochemical Reactions

Photochemical reactions are those reactions which take place in the presence of light (Photons). Combination of hydrogen and chlorine in presence of light to form hydrogen chloride is a typical example.

$$H_2(g) + C1_2(g) \xrightarrow{\text{light}} 2HCl(g)$$

(ii) Heterogeneous Reactions: A heterogeneous reaction means a reaction in whihc the reactants, products and the catalyst are present in different phases. Some of these reactions have been found to be of zero order. Two well known examples are,

(a) The decompsition of hydrogen iodide on the surface of gold.

(b) The decomposition of ammonia on the surface of tungsten, molybdenium or platinum at high temperatures.

Q11. Describe the various methods for determining the order of a reaction.

Ans :

Integration Method or Trial Method

This method consists in carrying out the reaction with known quantities of reactant(s) and determining the amount of reactant(s) consumed after different intervals of time and then substituting the data in the equations for first and second order reaction, derived earlier.

(i) Rate equations for first order reaction:

$$k = \frac{2.303}{t} \log \frac{C_0}{C}$$

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

(ii) Rate equation for second order reactions

$$k = \frac{1}{t}\left[\frac{1}{C} - \frac{1}{C_0}\right]$$

or $$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

The equation which gives constant value of k, the velocity constant, indicates the appropriate order of the reaction.

Alternatively, the validity of the various rate equations can be tested by the graphical method. Since the initial concentration C_0 or a is constant for each complete experiment, the equations for first and second order reduce to:

$$k = \frac{2.303}{t}\log(a-x) + \text{constant, for first order reactions}$$

$$k = \frac{1}{t}.\frac{1}{(a-x)} + \text{constant, for second order reactions}$$

(i) Thus, first order reactions will give a straight line when log (a – x) is plotted versus t.

(ii) While the second order reactions will give a straight line when 1/(a – x) is plotted versus t.

However the integration method suffers from the fact that it cannot determine the fractional order of recreations.

Half-life method (Fractional Change Method)

As discussed earlier half-life period of a reaction (i.e., the time required to convert the original concentration of the reactants to half) of different orders follows the following relationship.

For first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

For second order reactions

$$t_{1/2} = \frac{1}{ka}$$

Thus the half-life (or any definite fraction) period of a reaction is

(i) Independent of the initial concentration for a first order reaction.

(ii) Inversely proportional to the initial concentration in case of a second order reaction.

Thus, in general

$$t_e \propto \left(\frac{1}{a}\right)^{n-1}$$

Vant Hoff's Differential Method

The rate of reaction varies as the nth power of the concentration of the reactant where n is the order of the reaction. Thus, in general.

$$r = -\frac{dC}{dt} = kC^n$$

For two different concentrations C_1 and C_2, the rates r_1 and r_2 will be given by

$$r_1 = -\frac{dC_1}{dt} = kC_1^n$$

$$r_1 = -\frac{dC_2}{dt} = kC_2^n$$

On taking logarithms, we get

$$\log r_1 = \log k + n \log C_1$$

and $$\log r_2 = \log k + n \log C_2$$

On subtracting equation from equation, we get,

$$\log r_2 - \log r_1 = n \log C_2 - n \log C_1$$

$$\log r_2 - \log r_1 = n (\log C_2 - n \log C_1)$$

$$n = \frac{\log r_2 - \log r_1}{\log C_2 - \log C_1}$$

Thus in short the method involves the determination of concentration of reactant(s) at different intervals of time.

The values of r_1 and r_2 are evaluated by plotting cocnetration-time graphs corresponding to C_1 and C_2 concentrations. Substitution f these values in equatio leads to evaluation of the value of n.

Ostwald's isolation method

This method is applicable for reactions involving two or more reactants. In this method, the experiment is carried out for a number of times, each time taking all the reactants, except one, in excess, turn by turn. The reactant which is not taken in excess, is said to be isolated. The kinetics of the reaction then gives the order of the reaction with respect to the isolated reactant. The orders found for the different reactants are then added up to get overall order of the reaction.

Consider a reaction involving three reactants X, T and Z. Further let the order of the reaction be n, when X is isolated, n_2 and Y is isolated and n_3 when Z is isolated. Thus overall order of the reaction will be $n_1 + n_2 + n_3$.

Q12. Explain the effect of temperature on reaction rate.

Ans :

The ratio of the velocity constants of a reaction at two temperatures separated by 10°C is known as the temperature coefficient. The temperatures usually selected for this purpose are 25°C and 35°C. Thus mathematically,

$$\text{Temperature coefficeint} = \frac{\text{Velocity constant at 35°C}}{\text{Velocity constant at 25°C}} = \frac{k_{35}{}^{\circ}}{k_{25}{}^{\circ}}$$

For example, the temperature coefficients for dissociation of HI, and for the reaction between methyl iodide and sodium ethoxide are 1.8 and 2.9 respectively.

$$2HI \longrightarrow H_2 + I_2$$

$$CH_3I + C_2H_5ONa \rightarrow CH_3OC_2H_5 + NaI$$

Furthermore, greater the difference in temperature greater will be the difference in reaction rates. For example, increase of 160°C in temperature during the decomposition of acetaldehyde increases the reaction rate by 453 times. Similarly, the rate of decomposition of acetone dicarboxylic acid goes up by 220 folds for a 60° rise in temperature.

$$\underset{\text{Acetone dicarboxylic acid}}{HOOC-CH_2.CO.CH_2.COOH} \rightarrow \underset{\text{Acetone}}{CH_3.CO.CH_3} + 2CO_2$$

The increase in reaction rate with the increase in temperature is explained on the basis of collision theory. According to collision theory although a reactant molecule collides with another reactant molecule a billion times (10^9 times) per second, only those collisions which possess a certain minimum amount of energy result in chemical reaction. This minimum amount of energy which must be associated with molecules so that their mutual collisions result in chemical reaction is called threshold energy.

Number of molecules at T_1 having high kinetic energy $\propto$ Area of curve cedf.

$\therefore$ Increase in number of molecules due to increase of temp. from T_1 to T_2 $\propto$ Area of abfe.

The excess energy acquired by the reacting molecules is known as activation energy, i.e.,

Activiation energy = Threshold energy – Actual energy possessed by molecules.

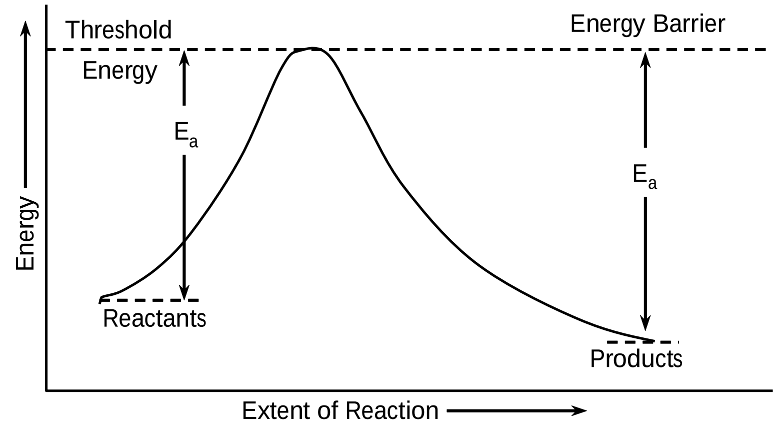


Fig.: Concept of Energy Barrier in chemical reaction

A reaction which has a higher activation energy is slow at ordinary temperatures; 'while the reaction, having lower activation energy will proceed at a faster rate at a given temperature. Thus difference in activation energy is mainly responsible for observed difference in rates of reactions.

Calculation of Activation Energy

According to Arrhenius, activation energy of a reaction with k as the rate constant and at temperature T may be given by the following empirical equation.

$k = Ae^{-E_a/RT}$

A = Constant, known as frequency factor

E_a = Activation energy of the reaction

R = Gas constant

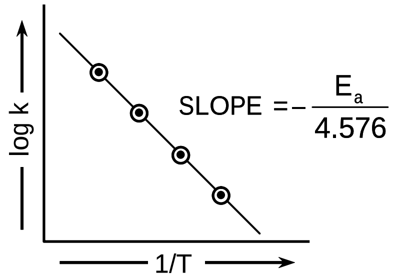
T = Temperature on absolute scale

e = 2.718

The values k_1 and k_2 of a reaction at tempeatures T_1 and T_2 are related by the following relation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Alternatively, the value of E_a can be evaluated by plotting a group between log k and $\frac{1}{T}$. The graph will give a straight line whose slope is equal to $-\frac{E_a}{2.303\,R}$ or $\frac{E_a}{4.576}$, from which the value of E_a can be determined.



Q13. Write a note on collision theory.

Ans :

There are two theories of reaction rates : (i) collision theory and transition state theory.

The Collision Theory

As mentioned earlier the chemical reactions occur only when the molecules collide with each other. Let us consider a reaction between two reactants A and B; n_a and n_b being the number of moles per unit volume of A and B, respectively. Since, the number of collisions per unit volume is directly proportional to the concentration, the total number of collisions (Z') per unit volume of the reactants will be given by

$$Z' = V\, n_a\, n_b \qquad \text{where V is a constant.}$$

In case, each collision results in chemical reaction, then the rate constant (k) of the reaction is obtained by dividing the number of collisions by the product of the concentration.

$$k = \frac{Z'}{n_a . n_b} = V$$

The number of collisions (Z') between the two reactants at any given concentration and temperature can be determined from the kinetic theory of gases. However, the values of k obtained by the above equation have been found to be very high than the expenmental values. This leads to the fact that each collision does not result in a chemical reaction and collision between only those molecules which possess a certain minimum amount of energy, known as the threshold energy, results in chemical reaction, such molecules are known as activated molecules. The difference between the threshold energy and the average energy possessed by these molecules is known as the activation energy On the basis of the activation energy, the number of activated molecules and thus the rate constant of the reaction can be calculated.

On the base of the kinetic theory of gases if there are n molecules per c.c. of the reactant (e.g. HI), the total number of colliding molecules per c.c. per second (Z) will be given by,

$$Z = \sqrt{(2)}\ \pi\nu\sigma^2 n^2$$

$$q = \frac{\text{Number of activated molecules}}{\text{Total number of molecules}}$$

$$= \frac{n'}{n}$$

$$q = e^{-E_a/RT}$$

Hence $\quad k = Ze^{-E_a/RT}$

Note that equation is similar to Arrhenius equation, *i.e.*,

$$k = Ae^{-E_a/RT}$$

The two equations, *viz*., equation and equation become identical if $A = Z$. Since Z gives the number of molecules colliding per c.c. per second, which is twice the number of collisions per c.c. per second (i.e., $Z = 2Z'$).

Q14. Describe the transition state theory.

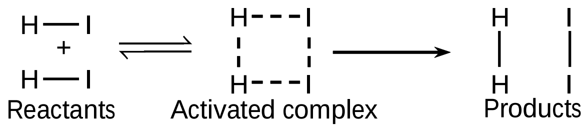
Ans :

The transition state theory (Absolute reactioh rate theory) or activated Simplex theory

According to this theory the reactant molecules are not directly converted into product but they are first transformed into an intermediate energy rich activated complex or transition state having only a transient existence. The activated complex subsequently breaks up to produce the products; the rate of decomposition of the activated complex determines the rate of reaction. Schematically,

$$\text{Reactant} \rightleftharpoons \text{Activated complex} \longrightarrow \text{Products}$$

For example,



The activation energy (E_a) of the reaction with reference to this theory is defined as the additional energy which the reactant mohcules must acquire to form the intermediate activated complex.

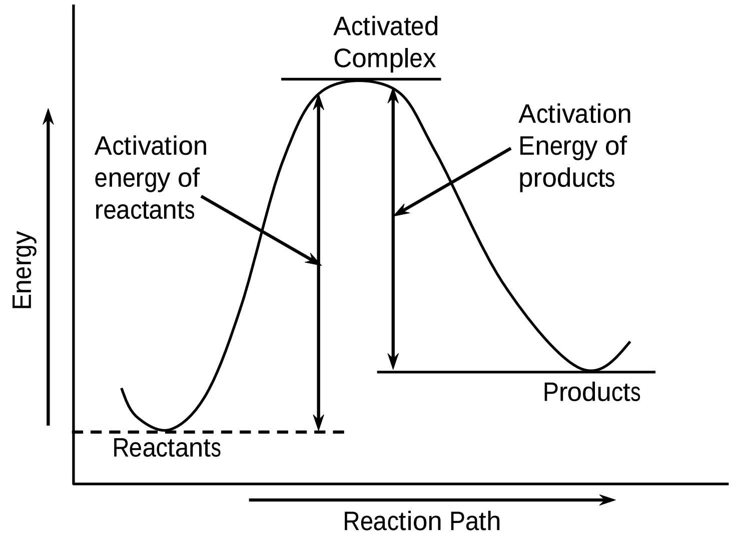


Fig.: Energy Changes during the reaction path

From the above figure it is clear that in the initial stage there is a small fall in the potential energy of the reactants. This is believed to be due to approach of the reactant molecules close to one another before reacting to form the activated complex. Similarly, in the final stage there is a small rise in energy of the products which is due to falling apart of the product molecules after the reaction.

The products possess higher energy than the reactants, the reaction will be endothermic. In such reactions the activation energy of the back reaction will always be less than that of the forward reaction. Activation energy of the back reaction means the additional energy which the product molecules must acquire to form the activated complex.

S4-P-2: PHOTOCHEMISTRY

Q15. Define photochemistry. Give any two differences between thermal and photochemical reactions.

Ans :

The branch of chemistry which deals with the absorption of light radiations and its effect (physical or chemical) on the substance is known as photochemistry. Wavelength between 2000 Å to 8000 Å.

Thermochemical reactions	Photochemical reactions
1. These reactions involve absorption or evolution of heat.	1. These reactions involve absorption of light.
2. They can take place even in the dark.	2. The presence of light is the primary condition for the photochemical process.
3. The free energy change (ΔG) of a thermochemical reaction is always negative.	3. The free energy change (ΔG) of most of photochemical reactions is negative, but it is positive in some cases.

Q16. State Grotthus - Draper law.

Ans :

Grotthus-Draper Law

This law is also called the principle of photochemical activation. It was put forward by Grotthus (in 1818) on theoretical grounds and confirmed by Draper (in 1839) by experiments; hence it was named as Grotthus-Draper law. It sates that 'only radiations of light which are absorbed by the substance are effective in producing a photochemical change'. In other words there cannot be a photochemical change unless some radiation is absorbed.

The absorbed light may simply be converted into heat e.g., in case of potassium permanganate solution, although the light energy is absorbed strongly, no chemical change is produced.

The absorbed light may be re-emitted as light of different wavelengths causing phenomenon like fluorescence, phosphorescence, etc.

Sometimes the absorbed light is transferred from one substance to another (both present together) which then undergoes some chemical change. This process is called photosensitization and the substance which initially absorbs light and then transfers it to the reaching substance(s) is known as sensitizer.

Photosynthesis of carbohydrates in plants where chlorophyll acts as a photosensitizer. This law is sometimes referred to as the first law of photochemistry.

Q17. Define stark - Enistein's law of equivalence.

Ans :

Stark-Einstein's Law of Photochemical Equivalence

This is also called the principle of quantum activation or the second law of photochemistry. This law correlates the extent of photochemical reaction with the amount of light energy absorbed. It was put forward by Einstein (1905) and Stark (1908) and states that in a photochemical reaction, each atom or molecule of a reacting substance absorbs one quantum of radiation (one Photon).

If ν is the frequency of the absorbed radiation, then the energy absorbed by each reacting atom or molecule is one quantum, i.e.,

$$E = h\nu \quad \text{... (i) (Energy absorbed by each reacting atom)}$$

Where h is Planck's constant.

Thus energy absorbed by 1 mole of the reacting molecules.

$$E = N\,hv$$

When N is Avogadro's number, i.e., the number of molecules present in 1 mole of the substance.

Substituting the value of v by c/λ, we get

$$E = N\,h\frac{c}{\lambda}$$

$$\left(\because \nu = \frac{c}{\lambda}\right)$$

Q18. Explain the term quantum efficiency (or) quantum yield.

Ans :

According to Einstein's law of photochemical equivalence, every reacting molecule absorbs one quantum of radiation and thus the number of reacting molecules should be equal to the number of quanta absorbed.

The relation between the number of quanta absorbed with the number of reacting molecule is usually expressed by the term quantum efficiency or quantum yield (ϕ). It is given by the formula.

$$\phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta absorbed in the same time}}$$

$$= \frac{\text{No. of moles reacting in a given time}}{\text{No. of einsteins absorbed in the same time}}$$

Quantum efficiency may be defined as the ratio of the number of moles undergoing reaction to the number of einsteins absorbed in the same time or it may be defined as the number of moles reacting per einstein of the light absorbed, quantum efficiency should be equal to unity.

Q19. Give reason for the very high quantum yield of $H_2 - Cl_2$ reaction.

Ans : **(Imp.)**

The quantum yield is found to be higher than 1 and in some cases it is lower than 1. The quantum yield higher than 1 or lower than 1 is collectively called as abnormal quantum yield. Quantum yields of some of the common photochemical reactions are

$H_2 + Cl_2 \rightarrow 2HCl$	4000 – 4360	10^6
$2HBr \rightarrow H_2 + Br_2$	2070 – 2530	0.01
$2HI \rightarrow H_2 + I_2$	2070 – 2530	2.0

The higher yield (more than 1) is due to the fact that one quantum of radiation brings about transformation of more than one molecule of the reactants. This generally happens for reactions where secondary processes like free radical and recombination reactions are possible. Here the photochemically activated molecule initiates a chain of reactions with the result several molecules undergo reaction although only one quantum of light is absorbed by the reactant ultimately leading to high quantum yield.

Q20. Explain the reason for the low quantum yield of $H_2 - Br_2$ reactions.

Ans :

The low quantum yield (i.e., reactions in which the number of molecules undergoing chemical change is too less than one per photon absorbed) is due to following three reasons:

(i) Deactivation of the photochemically excited molecules before they react.

(ii) Insufficiency of the absorbed quantum to activate some of the reacting molecules.

(iii) Recombination of some of the dissociated fragments of the excited molecule to give back the original molecule.

Those reactions in which quantum yield is simple interger such as 1, 2, 3, etc. Dissociation of HI and HBr.

Q21. Discuss the terms in Jablanski diagram.

Ans : **(Imp.)**

The Jablonski diagram is a pictorial representation of the energy transitions caused by the absorption of a UV radiation by a molecule. When a molecule absorbs a UV radiation, it is excited to one of the excited singlet electronic states (S_1 or S_2). Most promotions are from S_0 to the S_1, state; promotions to S_2 and higher singlet states take place, but in liquids and solids these higher states usually drop very rapidly to the S_1 state (about 10^{-13} to 10^{-11} sec.) The energy lost when an S_2 or S_3 molecule drops to S_1 is given up in small instalments to the environment by collisions with neighbouring molecules. Such a process is called an energy' cascade. Therefore in most cases the lowest vibrational level of the S_1 state is the only important excited singlet state. This state can undergo various physical and chemical processes.

(i) The molecule returns to its ground state either by emitting, .radiation (fluorescence) or by giving up its energy as heat (internal conversion). The fluorescent light is of slight lower energy (and so of longer wavelength) than the absorbed light.

(ii) The energy of excitation is transferred to another molecule, which is raised to an excited singlet level.

(iii) It may undergo crossing to the first excited triplet state (T_1). The transition from excited singlet to excited triplet state is radiationless and requires less than 10^{-9} sec. It is called a process of intersystem crossing. The first excited triplet state is generally of lower energy (hence more stable) than the first excited singlet state: therefore, inter system crossing is an energetically downhill process. However, after some time (10^{-4} sec. to several minutes), the triplet state also decays to the ground state by emitting a photoon of light whose wavelength is substantially longer than the wavelength of the radiation initially absorbed. (because ot the lower energy of the triplet state). This process is called phosphorescence. Like excited singlets, excited triplets can decay to the ground state by radiationless processes due to collision with solvent, with the vessel walls or with other molecules.

(iv) In special case, the excited molecule dissociates instead of vibrating.

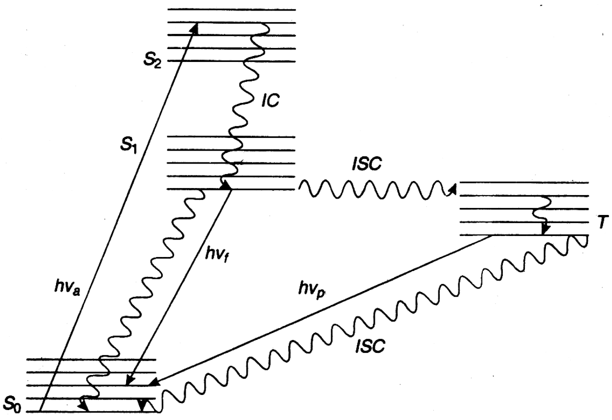


Fig.: Modified Jablonski diagram showing transitions between excited states and the ground state. Radiative processes are shown by straight line, radiationless process by wave lines

hv_a = Absorbed energy

hv_f = Energy lost as fluorescent light

1C = Internal conversion

hv_p = Energy lost as photophosphorescent light

ISC = Intersystem crossing

(v) Although both singlet and triplet states can undergo chemical reactions, they are much more common for triplets, because of their more stability. Excited singlet species, in most cases, have a lifetime of less than 10^{-10} sec, and undergo one of the physical processes already discussed before they have a chance to react chemically. Therefore, photochemistry is largely the chemistry of triplet states.

Q22. Discuss the photochemistry of $H_2 - Cl_2$ and $H_2 - Br_2$ reactions?

Ans : **(Imp.)**

1. Photochemical combination of hydrogen and bromine to form hydrogen bromide

The photochemical combination of hydrogen and bromine requires radiation less than 5100 Å for the primary process (excitation of bromine molecule to form bromine atoms).

$$Br_2 + hv \rightarrow Br + Br \qquad \text{(primary process)}$$

The quantum efficiency of the reaction is very low, i.e., about 0.01 at ordinary temperature. The low quantum efficiency is due to following secondary processes:

$$\left.\begin{array}{l} \text{(i) } Br + H_2 \xrightarrow{\text{endothermic}} HBr + H \\ \text{(ii) } H + Br_2 \xrightarrow{\qquad\qquad} HBr + Br \\ \text{(iii) } H + HBr \xrightarrow{\qquad\qquad} H_2 + Br \\ \text{(iv) } Br + Br \xrightarrow{\qquad\qquad} Br_2 \end{array}\right\} \text{Secondary Pr ocesses}$$

The above reactions indicate that

(a) The Br atom formed in the primary process combines with hydrogen molecule forming HBr and hydrogen atom [reaction (i) of secondary process].

(b) The hydrogen atom formed in the (i) equation combines with the fresh molecule of Br_2 forming more HBr and bromine atom reaction (ii) of secondary process. The bromine atom so formed may further react as in eq. (i) and thus reactions (i) and (ii) should repeat over and again, *i.e.,* chain reaction should be set up and the quantum yield for the reaction ($H_2 + Br_2 \rightarrow 2HBr$) should be very high. But actually the quantum yield is very low.

The low quantum yield of the reaction is due to highly endothermic nature of the reaction due to which it requires high energy of activation and hence takes inlace very slowly at ordinary temperature. they combine together to give back Br_2 molecule/Consequently, the quantum yield of the reaction is very low at ordinary temperature. The quantum yield of the above reaction increaes with increase of temperature.

2. Photochemical combination of hydrogen and chlorine

In contrast to the photochemical combination of hydrogen and bromine, the quantum yield of photochemical combination of hydrogen and chlorine is extremely high of the order of 10^4 to 10^6.

$$H_2 + C1_2 \xrightarrow{h\nu} 2HCl \quad \phi = 10^4 \text{ to } 10^6$$

The high quantum yield of this reaction is due to chain mechanism proposed by Nernst (in 1918). Like other photochemical reaction, the complete reaction involves two processes:

(a) Primary process

The chlorine molecule absorbs one quantum of light of wavelength below 4800 A and dissociates to give two chlorine atoms.

$$Cl_2 + h\nu \rightarrow 2Cl$$

(b) Secondary process

As soon as chlorine atoms are formed, following secondary processes take place.

$$\left.\begin{array}{l}\text{(i) } Cl + H_2 \xrightarrow{\text{Exothermic}} HCl + H \\ \text{(ii) } H + Cl_2 \xrightarrow{\text{Exothermic}} HCl + Cl\end{array}\right\}\text{Chain Propagating Steps}$$

Chlorine atom formed in the (ii) equation reacts with fresh molecule of H_2 [as in eq. (i)] forming HC*l* and hydrogen atom and thus the reactions (i) and (ii) repeat over and again until almost whole of hydrogen and chlorine have reacted to form HC*l*. These two reactions, hence are called chain propagating steps; and the reaction of primary process is called as chain initiating step since it is this step which produces chlorine atom responsible for chain propagation.

The chain of the reactions (i) and (ii) may be terminated by the combination of chlorine atoms to form chlorine molecule. This reaction takes place on the walls of the reaction vessel.

(iii) It is interesting to note that although the mechanism of the above reaction is similar to that of the photochemical combination of H_2 and Br_2, yet the quntum yield of the two reactions differ very much. The difference is due to difference in reaction (i) of the secondary process. Reaction (i) of the secondary process is highly endothermic incase of photochemical combination of H_2 and Br_2 and hencelakes place very slowly while the corresponding reaction in case of H_2 and Cl_2 is exothermic and takes place almost instantaneously.

Short Question and Answers

1. Define rate of a reaction and order of reaction.

Ans :

Rate of Reaction

Rate of reaction as the decrease of concentration of the reactant(s) or increase in concentration of the product(s) per unit time. Mathematically, the rate of reaction can be expressed as below:

$$\text{Rate of reaction} = \frac{\text{Amount of reactant consumed}}{\text{Time interval}}$$

or $$\text{Rate of reaction} = \frac{\text{Amount of product produced}}{\text{Time interval}}$$

Order of reaction

The order of reaction can be defined as the sum of the power of the concentration terms.

Although most of the reactions have a whole number order, certain reactions having fractional orders (e.g., 1/2, 3/2, etc.) are also known. For example, the order of reaction of the ortho-para hydrogen conversion is 3/2 since its rate is expressed as below:

$$\frac{dx}{dt} = k[H_2]^{3/2}$$

Similarly, the order of dissociation of acetaldehyde in the gas phase is 3/2.

$$\frac{dx}{dt} = k[CH_3CHO]^{3/2}$$

2. Write the effect of temperature in a rate of reaction.

Ans :

The rate of chemical reaction increases as the temperature is raised. Consequently, reactions are carried out at elevated temperatures so that a good yield of the products can be obtained in a reasonable time.

3. What is Half-life Period of a First Order Reaction ($t_{1/2}$)

Ans :

The equation (vi) can also be used to calculate the time taken for any given proportion of the reactant to disappear. In general, half-life period of a reaction is the time required to convent the concentration ($C_0/2$). Thus by substituting the value $C_0/2$ in place of C in equation (vi), the half-life of the reaction can be ascertained.

$$t_{1/2} = \frac{2.303}{k} \log \frac{C_0}{C_0 / 2}$$

$$= \frac{2.303}{k} \log 2 \qquad (\log 2 = 0.313)$$

$$= \frac{0.693}{k}$$

---

4. What are pseudo molecular reactions? Give one example.

Ans :

Hydrolysis reactions in neutral or acid solution are also of first order. This is because the amount of water used greatly exceeds that required for the reaction, while the acid acts as a catalyst and is, therefore, not used up during the reaction. Some examples are cited below.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{acid}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

---

5. What is Half-life Period of a Zero order reaction ($t_{1/2}$)

Ans :

The expression for the half-life period (i.e., time taken for converting the original concentration of the reactants to one half) may be obtained as follows:

When $x = \frac{a}{2}, t = t_{1/2}$

where "a" is the initial amount, i.e., when t = 0, and x is the amount reacted at time t which is $t_{1/2}$ in case of half-life period.

Substituting the value of x and t in the zero order reaction,

$$x = kt$$

$$\frac{a}{2} = k \times t ½$$

$$t_{1/2} = \frac{a}{2k}$$

---

6. Give the examples of Zero order reactions.

Ans :

Two types of reactions have been found to be of zero order.

(i) Photochemical Reactions

Photochemical reactions are those reactions which take place in the presence of light (Photons). Combination of hydrogen and chlorine in presence of light to form hydrogen chloride is a typical example.

$$H_2(g) + C1_2(g) \xrightarrow{\text{light}} 2HCl(g)$$

(ii) Heterogeneous Reactions

A heterogeneous reaction means a reaction in whihc the reactants, products and the catalyst are present in different phases. Some of these reactions have been found to be of zero order. Two well known examples are,

(a) The decompsition of hydrogen iodide on the surface of gold.

(b) The decomposition of ammonia on the surface of tungsten, molybdenium or platinum at high temperatures.

7. What is the term quantum efficiency (or) quantum yield?

Ans :

According to Einstein's law of photochemical equivalence, every reacting molecule absorbs one quantum of radiation and thus the number of reacting molecules should be equal to the number of quanta absorbed.

The relation between the number of quanta absorbed with the number of reacting molecule is usually expressed by the term quantum efficiency or quantum yield (ϕ). It is given by the formula.

$$\phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta absorbed in the same time}}$$

$$= \frac{\text{No. of moles reacting in a given time}}{\text{No. of einsteins absorbed in the same time}}$$

8. Write the differences between thermal and photochemical reactions.

Ans :

Thermochemical reactions	Photochemical reactions
1. These reactions involve absorption or evolution of heat.	1. These reactions involve absorption of light.
2. They can take place even in the dark.	2. The presence of light is the primary condition for the photochemical process.
3. The free energy change (ΔG) of a thermochemical reaction is always negative.	3. The free energy change (ΔG) of most of photochemical reactions is negative, but it is positive in some cases.

9. What is photosensitization? Give one example.

Ans :

Photosensitization

The absorbed light is transferred from one substance to another (both present together) which then undergoes some chemical change. This process is called photosensitization and the substance which initially absorbs light and then transfers it to the reaching substance(s) is known as sensitizer.

Ex: Photosynthesis of carbohydrates in plants where chlorophyll acts as a photosensitizer. This law is sometimes referred to as the first law of photochemistry.

Choose the Correct Answers

1. The velocity constant of a rection is given by expression [a, b, c]

   Rate = $k[A]^2 [B]$

   the reaction is of

   (a) First order with respect to B (b) Second order with respect to A

   (c) First order, overall (d) Third order, overall

2. The specific rate constant of a first order reaction depends on the [d]

   (a) Concentration of the reactant (b) Concentration of the product

   (c) Time (d) Temperature

3. A zero - order reaction is one [a, b]

   (a) Whose rate is not affected by concentration

   (b) In which concentration of the reactants does not change with time

   (c) In which reactants do not react

   (d) In which one of the reactants is in large excess

4. What will be amount of $^{128}I_{53}$ ($t_{1/2}$ = 25 minutes) left after 50 minutes [c]

   (a) One-half (b) One-third

   (c) One-fourth (d) One-eighth

5. Which of the following rate laws has an overall order of 0.5 for the reaction involving substances X, Y and Z [c]

   (a) Rate = $k[C_x] [C_y] [C_z]$ (b) Rate = $k[C_x]^{0.5} [C_y]^{0.5} [C_z]^{0.5}$

   (c) Rate $k[C_x]^{1.5} [C_y]^{-1} [C_z]^0$ (d) Rate = $k[C_x] [C_y]^0 [C_z]^2$

6. The temperature coefficient of most of the reactions lies between [b]

   (a) 1 and 3 (b) 2 and 3

   (c) 1 and 4 (d) 2 and 4

7. In which of the rate order reaction is independent of the initial concentration [b]

   (a) Zero order (b) First order

   (c) Second order (d) None of the above

8. Hydrolysis of methyl follows order of reaction [c]

(a) Zero order
(b) First order
(c) Second order
(d) None of the above

9. Units of zero order reaction [b]

(a) Time^{-1}
(b) Mole liter^{-1}.sec^{-1}
(c) Liter mole^{-1} time^{-1}
(d) None of the above

10. The increasing reaction rate with the increasing temperature is explained by [a]

(a) Collision theory
(b) Transition state theory
(c) Activation energy
(d) None of the above

11. Synthesis of starch by platns is an example of: [c]

(a) Photosensitization
(b) Photography
(c) Photosynthesis
(d) None of these

12. To high quantum yield of a photochemical reaction may be due to: [c]

(a) Activation of the molecule by energy supplied by other transient intermediates formed.
(b) Activation of molecule through fluoresecence or phosphoresence.
(c) Chain reactions caused by generation of atoms of free radicals in the primary process.
(d) None of these

13. The light emitted by a glow worm is an example of : [c]

(a) Fluorescence
(b) Phosphorescence
(c) Chemiluminescence
(d) None of these

Fill in the blanks

1. Decomposition of hydrogen peroxide [$2H_2O_2 \longrightarrow 2H_2O + O_2$] is a ________.
2. The order of reaction of inversion of cane sugar is ________ while its moleculariry is ________.
3. For the first order reaction half - life time is ________ on the initial concentration.
4. The life period of radioactive substance is x hour. The fraction remaining after 2nd hour is ________.
5. A reaction is said to be of ________ its rate is entirely independent of the concentration of the reactants.
6. Time reaction is said to be of ________ its rate is entirely independent of the concentration of the reactants.
7. Temperature coefficient of a reaction is determined by comparing velocity constants at two temperatures separated by ________.
8. The rate of reaction is measured either by the increase in the amount of ________ or by the decrease in the amount of ________ per unit interval of ________.
9. If doubling the concentration of a reactant X in a reaction $X + Y \longrightarrow$ product, increases the rate four times and tripling its concentration increases the rate nine times, this indicates that the rate of reaction is proportional to the ________ of the concentration of ________ and thus its rate is given by ________.
10. When rate $k[A]^2 [B]$, the reaction is said to be of ________ order in A and of ________ order in B. The order of the overall reaction will be the sum of the ________ of [A] and [B].
11. Quantum yeild is ________
12. The law of photochemical equivalence is valid only for ________ process of very photochemical reaction.
13. Quantum yield in $H^+_2 + Cl_2$ reaction ________.
14. Second law of photochemistry is known as ________.

ANSWERS

1. First order reaction
2. One, two
3. Independent
4. 1/4
5. Zero order
6. 10 times
7. 10°C
8. Products, reactants, time
9. Square, X, $K[X]^2$
10. Second, first exponents
11. $\dfrac{\text{No. of reacting atoms in a given time}}{\text{No. of quanta in the same time}}$
12. Primary
13. 10^{-6} ϕ
14. Stark - Einstein's law of photochemical equivalent.

One Mark Answers

1. What is chemical kinetics ?

Ans :

Chemical kinetics is the study of rate of chemical reaction. It involves studying the rate laws, rate of reactions, the factors influencing reaction rates and the mechanism involved in the progress of the reaction.

2. Find the order of a reaction form the following rate law $r = k[A]^2[B]$.

Ans :

Given that

$r = k[A]^2 [B]$

Order, $n = 2 + 1$

$= 3$

$\therefore n = 3$

3. The rate constant for a first order reaction is $0.005\ min^{-1}$. Calculate its half-life.

Ans :

Given that

$k = 0.005\ min^{-1}$

Half-life, $t_{\frac{1}{2}} = \dfrac{0.693}{k}$

$= \dfrac{0.693}{0.005}$

$t_{\frac{1}{2}} = 138.6$ min.

4. Identify the order of saponification of ester.

Ans :

Saponification of ester is hydrolysis of an ester in the presence of a base.

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Since two reactants are involved in the reaction its a second order reaction.

5. In which reactions the absorption of light takes place in primary process only ?

Ans :

Photochemical reactions

6. State Grothus draper law.

Ans :

According to Grothus - Draper's law, "Photochemical reactions in a molecule are produced by only those light radiations which are absorbed by the molecule".

7. The HBr reaction is said to have low quantum yield where as decomposition of HI has high. Comment.

Ans :

The quantum yield of HBr reaction is 0.01. That means the quantum yield is less than one $(\phi < 1)$. Hence it is said to have low quantum yield. While the quantum yield of decomposition of HI is 2 i.e., $\phi > 1$. Hence it has high quantum yield.

8. What are singlet and triplet state?

Ans :

The state where the total spin quantum number of unpaired electrons, $S = 0$ is a singlet state and a set of possible states where the total spin quantum number, $S = 1$ is a triplet state.

UNIT - IV

(General Chemistry)

S4-G-1: Theories of Bonding in Metals

Valence bond theory, Explanation of metallic properties and its limitations, Free electron theory, thermal and electrical conductivity of metals, limitations, Band theory, formation of bands, explanation of conductors, semiconductors n-type and p-type, extrinsic & intrinsic semiconductors, and insulators.

S4-G-2: Carbanions-II

Mannich reaction , Michael addition and Knoevengeal condensation Synthetic applications of Aceto acetic ester. Acid hydrolysis and ketonic hydrolysis: Preparation of ketones, monocarboxylic acids and dicarboxylic acids Malonic ester– synthetic applications. Preparation of (i) substituted mono carboxylic acids and (ii) substituted dicarboxylic acids.

S4-G-3: Colloids & Surface Chemistry

Definition of colloids. Classification of colloids. Solids in liquids (sols): preparations and properties – Kinetic, Optical and Electrical stability of colloids. Protective action. Hardy–Schultz law, Gold number. Liquids in liquids (emulsions): Types of emulsions, preparation and emulsifier. Liquids in solids(gels): Classification, preparations and properties, General applications of colloids.

Adsorption: Types of adsorption. Factors influencing adsorption. Freundlich adsorption isotherm. Langmuir theory of unilayer adsorption isotherm. Applications.

S4-G-1: THEORIES OF BONDING IN METALS

Q1. Explain the metallic properties and its Limitations by valence bond theory.

Ans :

Valence bond theory is explained by pouling. According to this theory, the structure of metals may be described in terms of covalent bonds that resonate among the alternate inter atomic positions in metals.

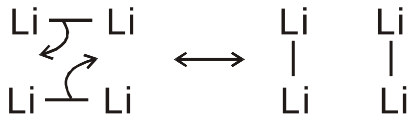
In a metal crystal, each atom is held to 8 or 12 more atoms. However, the metal does not possess sufficient valence electrons for the formation of electron pair bonds between itself (or) neighbouring atoms.

For example, consider the case of Lithium metal which crystallizes in a BCC. In this arrangement each lithium atom is in direct contact with 8 other lithium atoms. Thus each lithium atom must form covalent bonds with 8 other lithium atoms which require 16 electrons for the formation of localized electron pair bonds.

However, each lithium atom has only one valence electron and hence only 9 electrons are available for bond formation between 9 lithium atoms.

This discrepancy can only be explained on the bond that the covalent bonds between two lithium atoms are not localized but they are highly delocalized. In other words, each covalent bond between two lithium atoms resonate between various atoms in the metal.

Let us illustrate the phenomenon of resonance in metallic bonding by considering four lithium atoms. Since every lithium atom has only one valence electron, no lithium atom can form two bonds simultaneously. Hence whenever a bond between two atoms shifts, it is accompanied by the simultaneous shifting of the other bond between two other atoms(structure -I) to give structure-II.



I II

Explanation of properties of metals by VBT :

(i) The layers of mobile electrons provide easy passage for the electrons moving under an electrical potential gradient.This explains high electrical conductivity of metals.

(ii) When the temperature is raised, the freely moving electrons absorb energy at one end and pass it on all the atoms throught are the crystal lattice. This explain thermal conductivity of metals.

(iii) Since the charge distribution resulting from bonding is nearly uniform throughout the positive ions in the crystal, they may change their position relative to their neighbours without changing the internal environments. In other words, the shape is changed without breaking the crystal. This explains high maleability and ductility of metals.

(iv) The above point indicates that ions can change positons without breaking metallic crystal. Thus when a stress is applied, the structure will change temporarily and restored back on removing the stress. This explains why metals are highly elastic.

(v) The close packing of atoms in metallic crystal explains the high density of metals. The low density of few metals like Li, Be, Mg, etc, is due to their low atomic weights.

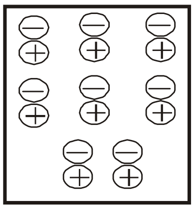
Limitations :

- The valence bond theory provides only a qualitative explanation of various metallic properties like electrical conductance, thermal conductance, high degree of malleability and ductility, high elasticity and high density.
- It fails to do so on a quantitative scale.
- The theory also does not explain metallic character in the liquid state or in solution.

Q2. Discuss the Free electron theory.

Ans : **(Imp.)**

Free electron theory was proposed by Drude and Lorentz. This theory explains the high electrical and thermal conductivities of metals. According to this theory the low ionization energies of metal atoms lose one or more of their valence electrons and change into cations. The lost electrons are not localized i.e., they move freely and randomly throughout the volume of the metal. Thus according to this view a metal may be regarded as an assembly of positive ions (cations) immersed in a sea of mobile electrons or a sea of negative charge cloud. The strong electrostatic attraction between the electron cloud and positive ions holds the crystal together, i.e., the valence electrons act as a glue to hold the metal ions in the lattice.



Structure of metallic crystal on the basis of free electron model

The free electron model of the metallic bonding explains the following characteristics of metals.

(i) According to free electron model, the metallic bond is delocalised and non-directional. In metallic system the bonds from any one atom are spherically distributed in all directions which accounts true close packing of metals.

(ii) Alkali metals are soft and have low melting point, while the transition metals are hard and have high melting point.

(iii) The presence of mobile valence electrons explains the high electrical and thermal conductivities of metals.

(iv) The ductility and malleability of the metals can also be explained due to non-directional nature of the metallic bond.

(v) Due to the presence of free electrons many metals emit electrons if heated to a high temperature & if exposed to a short wavelength radiations.

Limitations :

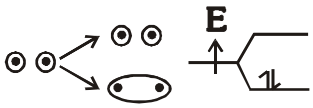
1. It does not clearly explain semi-conductance.
2. It does not explain the specific heats of metals.

Q3. Discuss in detail the Bond theory of metals.

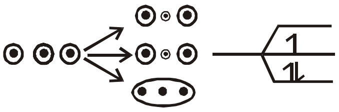
Ans : **(Imp.)**

Band theory is also called as molecular orbital theory of metals.According to this theory, the entire metal is cosidered as a big molecule and molecular orbitals obtained by the coalescence of the individual atomic orbitals cover the entire metal. When two atomic orbitals combine together, two molecular orbitals are formed. Similarly, coalescence of n atoms leads to the fomration of n molecular orbitals. The number of atoms in a particular crystal is very large, their combinations will give rise to as many molecular orbitals as the number of atoms. However, instead of producing a bonding and antibonding molecular orbital, as diatomic molecule does their combination produces a band of energy levels which are very close to each other. The electrons concerned with the interatomic bonding are not associated with individual atoms but are property of the entire energy band as a whole. Let us illustrate the whole theory by taking lithium metal ($1s^2$, $2s^1$) as an example.

When two atomic orbitals of lithium coalesce together, two molecular orbitals are formed, similarly coalescence of three atomic orbitals leads to the formation of three molecular orbitals.

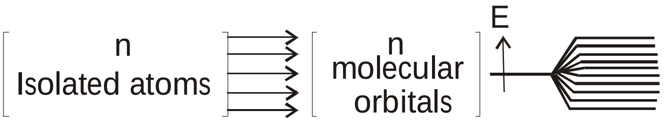


Formation of two MO's(Li_2)



Formation of three MO's(Li_3)

When ‘n’ AO’s of isolated lithium atoms coalescence to form ‘n’ MO’s. The n MO’s form a bond of closely spaced levels. An electron in any one of these orbitals is a property of the crystal as a whole and serves to bind various nuclei in the crystal together.



Formation of n MO’s from n lithium atoms

Q4. Write a short notes on Semiconductors.

Ans : **(Imp.)**

Semi conductors are those substances, which allows a portion of electric current to flow through them. At room temperature the electrical conductivity of a semiconductor lies between that of conductor and an insulator, it is in the range of 10^{-9} to 10^{2} ohm^{-1}. cm^{-1}.

Actually, semiconductors are those solids which are perfect insulators at absolute zero, but conduct electric current at room temperature.

Eg. Si and Ge

These are two types

a) Intrinsic semiconductors

b) Extrinsic semiconductors.

(a) Intrinsic semiconductors

At OK, pure ‘Si’ or ‘Ge’ acts as insulators because electrons fixed in coralent bonds are not available for conduction. But at higher temperature some of the covalent bonds are broken and the electrons so released become free to move in the crystal and thus conduct electric current . This type of conduction is known as intrinsic conduction.

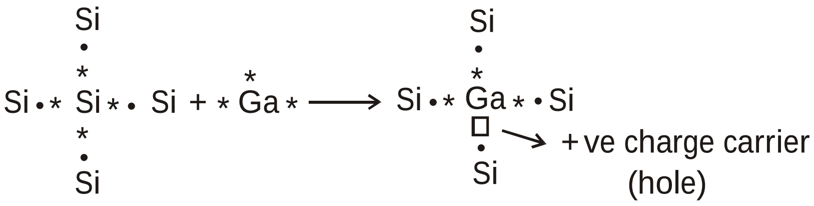
(b) Extrinsic semiconductors :

‘Si’ and ‘Ge’ (14 group elements) in pure state, have very low electrical conductivity. However, the electrical conductivity of these elements is greatly enhanced by the addition of even traces of an element belonging to group 13(III) or group 15 (V) to the crystals of group 14 (IV) elements, i.e., ‘Si’ and ‘Ge’. Introduction of group 15 and group 13 elements to the crystal lattice of group 14 elements (Si or Ge) produces n-type semiconductors and p-type semiconductors respectively.

(i) p-type semiconductors : (n stands for negative). This type of semiconductor is produced due to metal excess defect and by adding trace amounts of group 15 elements like P, As, Sb to the group 14 elements like ‘Si’ and ‘Ge’. ‘Si’ and ‘Ge’ have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. But 15 group elements P, As or Sb contain five valence electrons, they occupy some of the lattice sites in ‘Si’ or ‘Ge’ crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring ‘Si’ atoms. The fifth e^- extra and become delocalized. These delocalized e^-s increase the conductivity.

Since, no. of negatively charge carriers are more compared to positively charged carriers hence called n-type Semiconductors.

(ii) p-type semiconductors : Si /Ge are doped with Group (III) elements like B/Al/Ga, which possess 3 valence electrons.



Since no. of positively charged carriers are more compared to negatively charged carriers called p-type semiconductors.

Q5. Define conductors, Insulators and semiconductors.

Ans :

Conductors :

The solids with conductivities ranging between $10^4 - 10^7$ ohm^{-1}, cm^{-1} are called conductors.

Ex : Metalls

Insulators :

The solids with conductivities ranging between 10^{-20} to 10^{-10} $ohm^{-1}. cm^{-1}$ are called insulators.

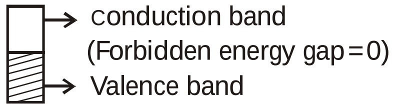
Ex : Rubber, plastics.

Semiconductors :

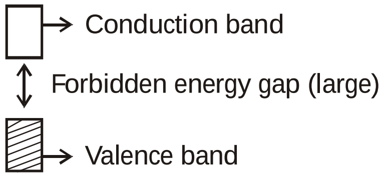
The solids with conductivities ranging between 10^{-6} to 10^4 are called as semiconductors

Ex : Si, Ge.

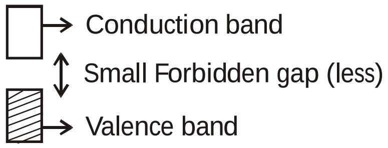
According to Band theory



Conductors



Insulators

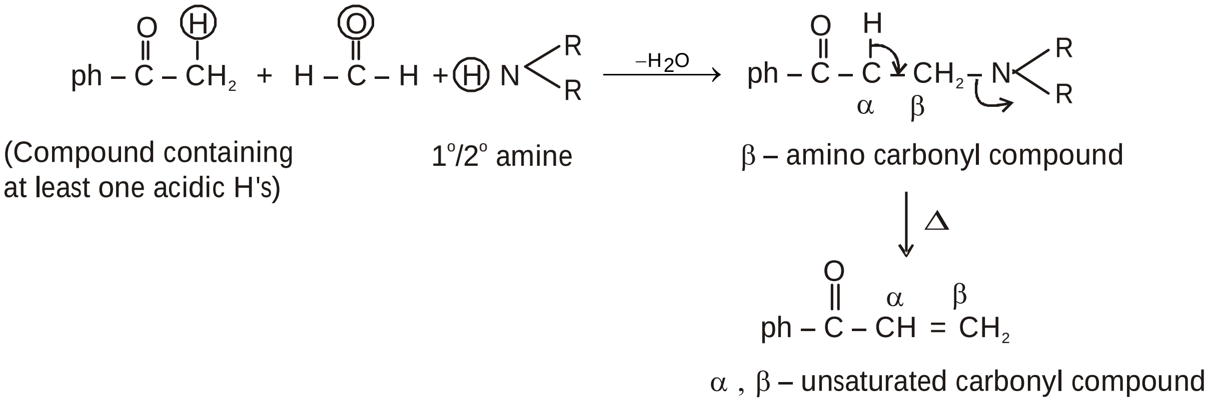


S4-G-2: CARBANIONS-II

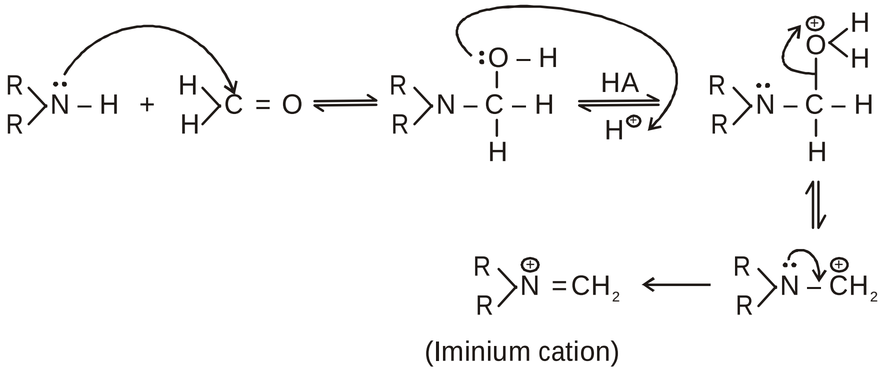
Q6. Explain mannich reaction with mechanism.

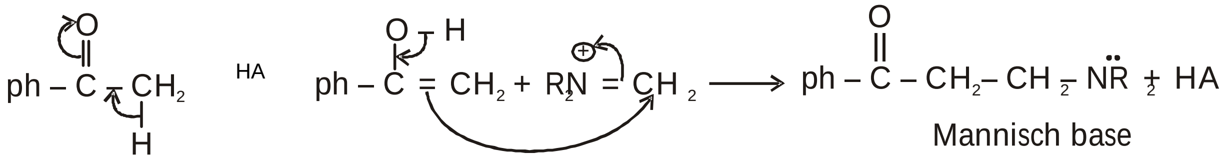
Ans :

Mannich reaction :



Mechanism :

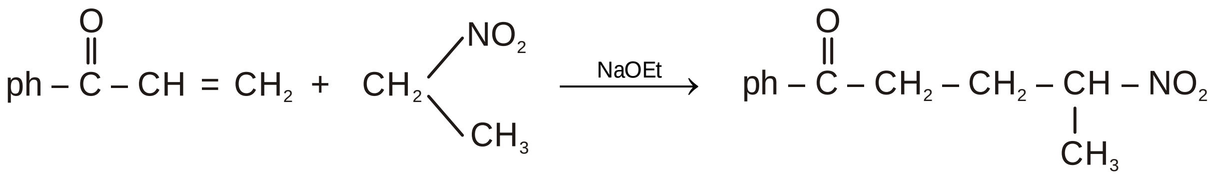




$$ph-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\ddot{N}R_2+HA$$

Q7. Explain Michel addition reaction with mechanism.

Ans :

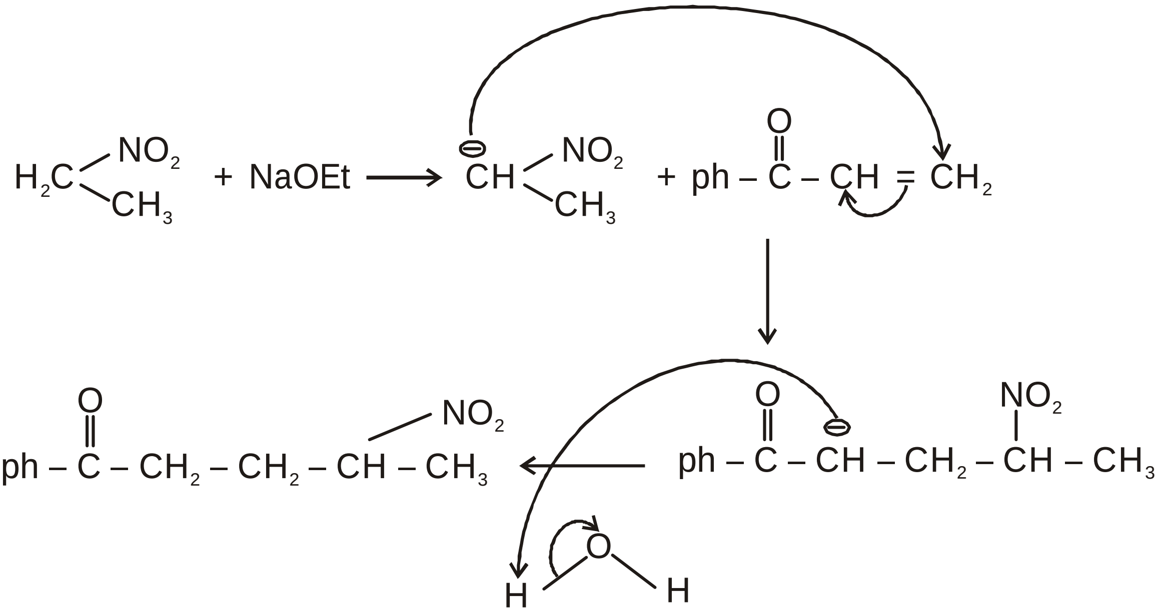


$$ph-\overset{O}{\overset{\|}{C}}-CH=CH_2+CH_2\begin{matrix}NO_2\\CH_3\end{matrix}\xrightarrow{NaOEt}ph-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-NO_2$$

α, β unsaturated carbonyl compound

Active methylene group

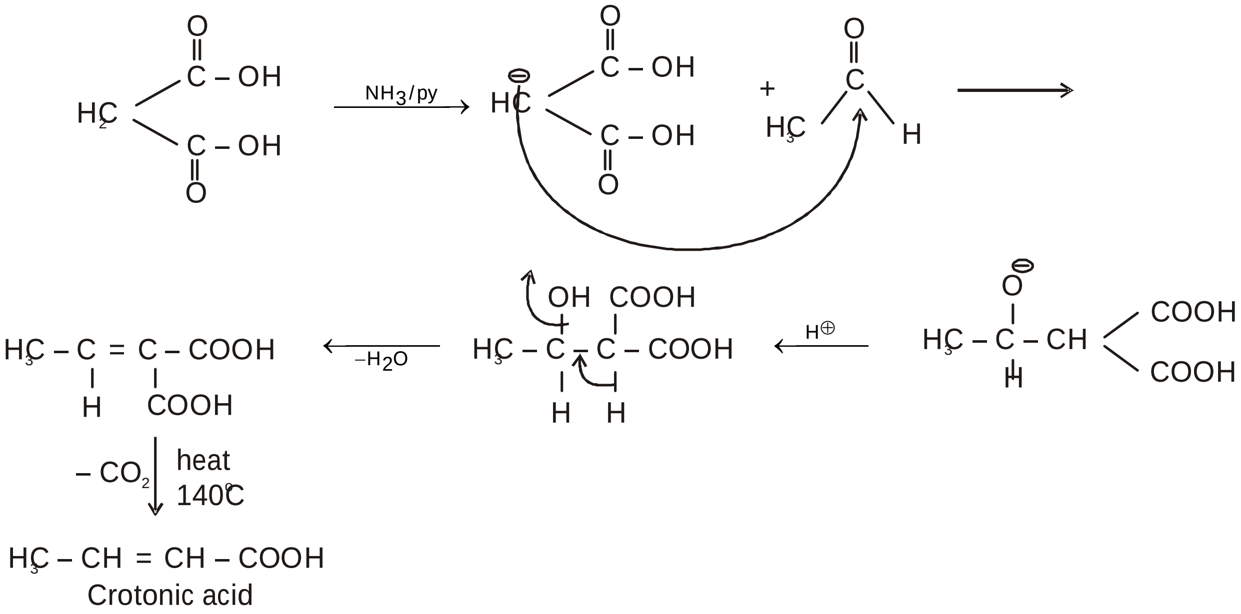
Mechanism :



Q8. Explain knoevengeal condensation reaction with mechanism.

Ans :

Nucleophilic addition of compound with active ‘H’ to a carbonyl compound followed by dehydration in presence of NH_3, amines, pyridine and piperidine etc to form α, β unsaturated compound.



Q9. Mention the synthetic applications of aceto acetic ester.

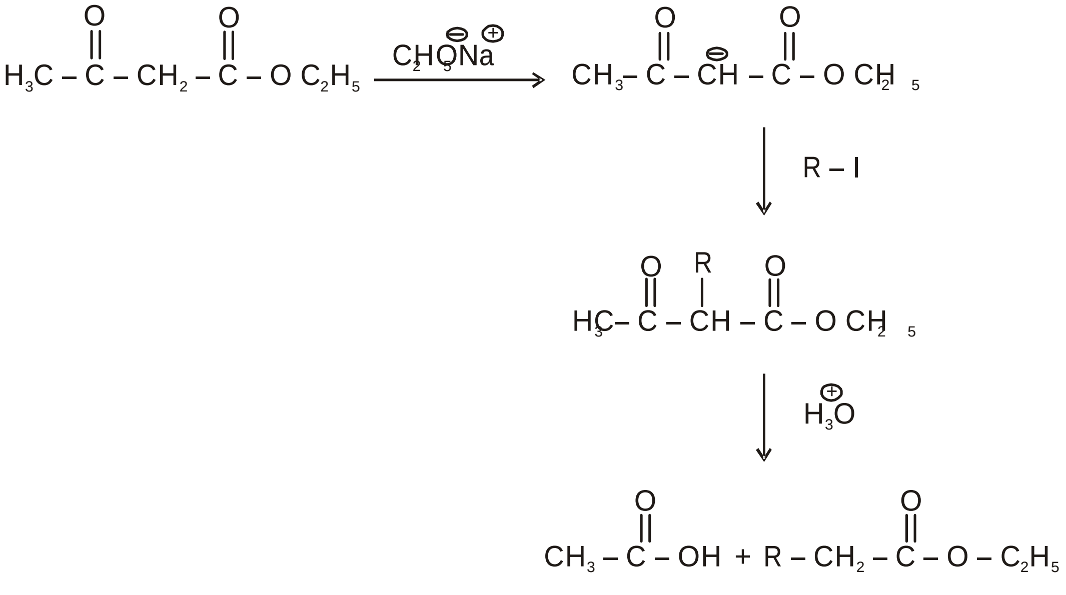
Ans : **(Imp.)**

Aceto acetic ester is an important tool in the hands of a synthetic organic chemist. It is used for the synthesis of a variety of carboxylic acid and ketones the synthetic importance is due to

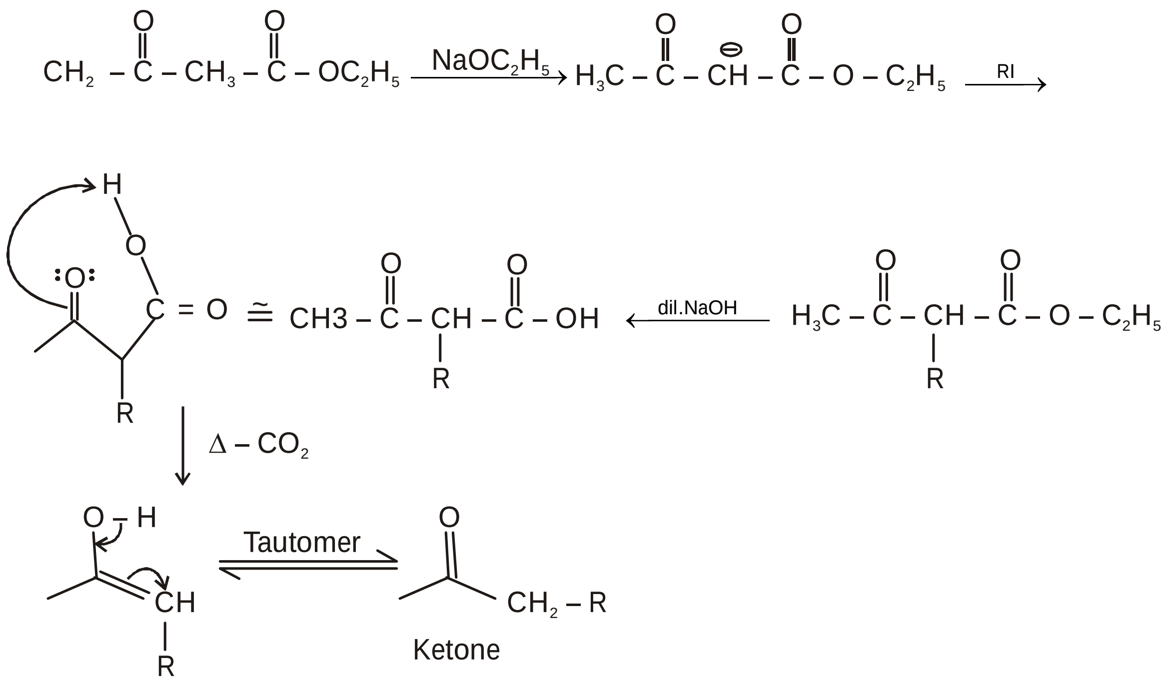
(i) The presence of an active methylene group whose one both hydrogen can be replaced by any group.

(ii) ability to undergo ketonic (or) acidic hydrolysis

Acidic hydrolysis :



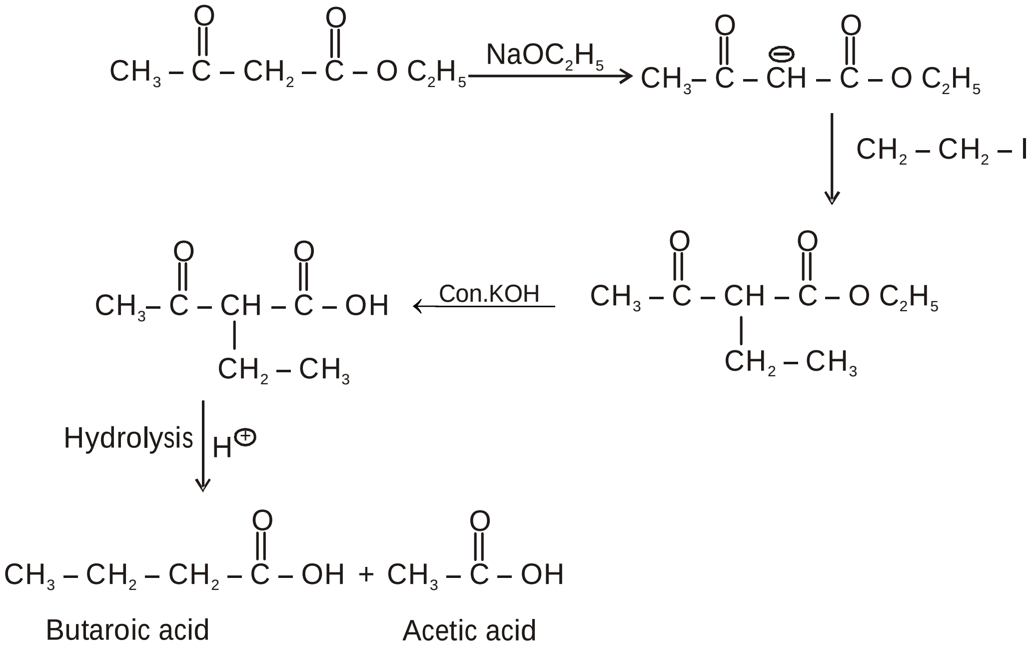
Ketonic hydrolysis



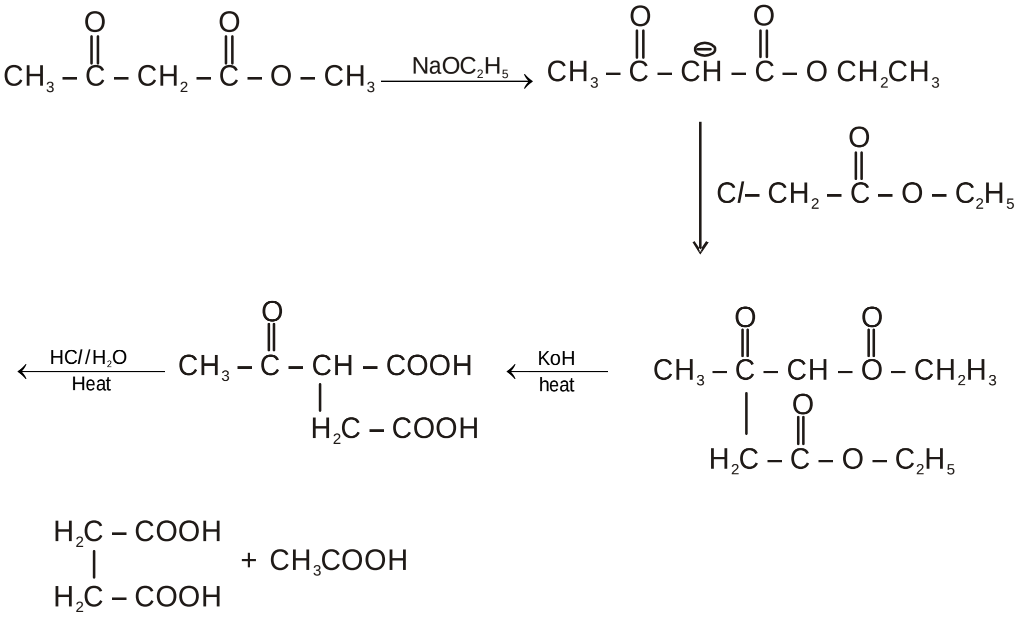
Q10. Write the preparations of monocarboxylic acid and dicarboxylic acids.

Ans :

Preparation of monocarboxylic acid :



Preparation & dicarboxylic acid :



Succinicacid

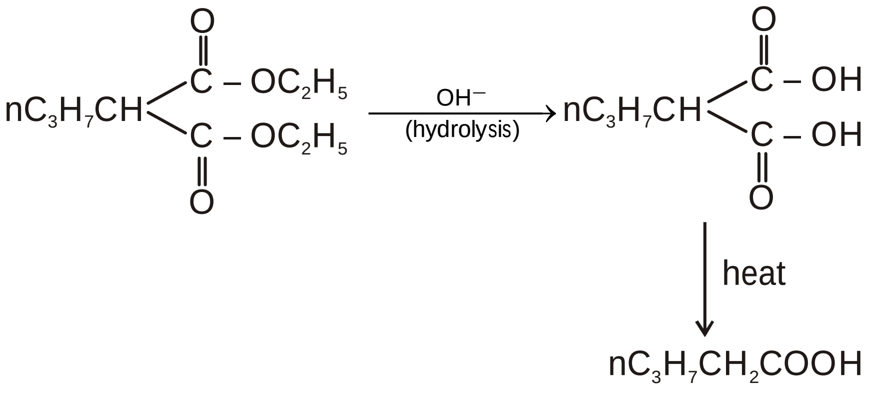
Q11. Explain the synthetic applications of malonic ester.

Ans :

Malonic ester and its mono and alkyl derivatives can easily be converted into acetic mono and di-alkyl acetic acids respectively.

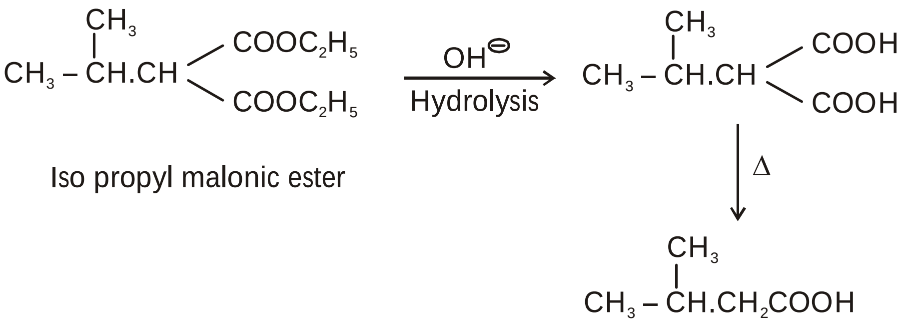
For example, systhesis of n-valeric acid (n - pentanoic acid or n-propyl acetic acid), Iso valeric acid and active valeric acid can be prepared as below

(i) Synthetic of n-valeric acid (n-propyl acetic acid)



n-valeric acid

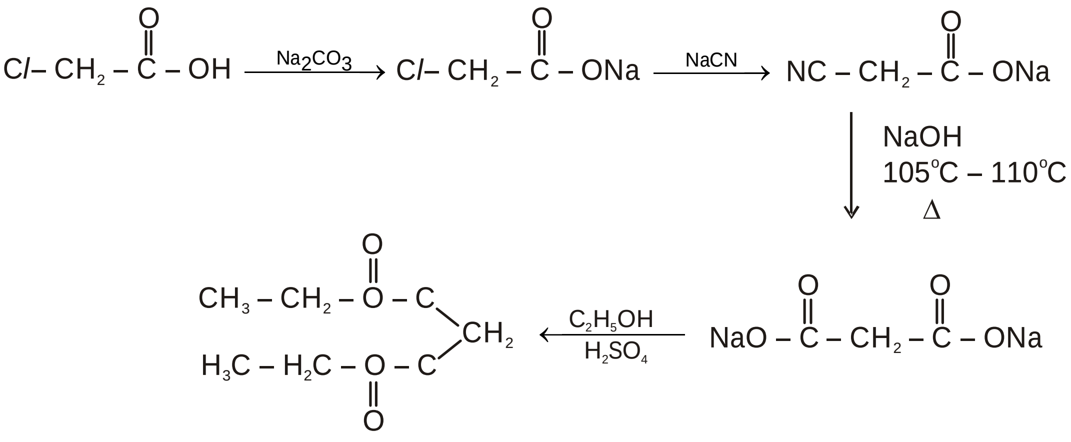
(ii) Synthesis of Iso valeric acid (Iso propylacetic acid)



Iso valeric acid

Q12. Write the preparation method for malonic ester and their synthetic applications.

Ans :



Diethyl malonate

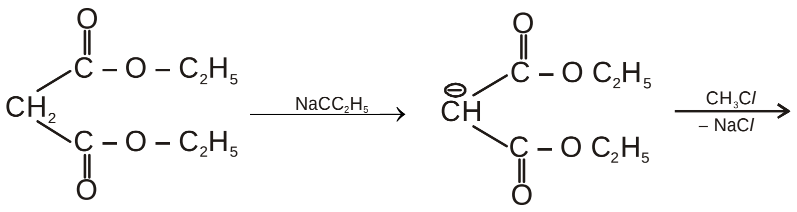
Synthetic applications :

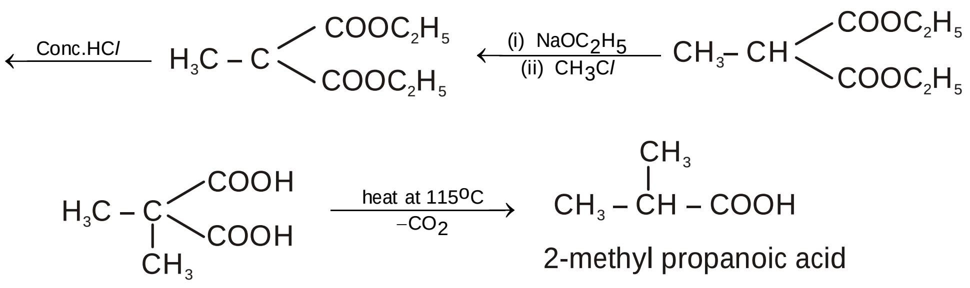
Malonic ester can be used in the preparation of substituted monocarboxylic acids and substituted dicarboxylic acids.

Q13. Write the preparations of substituted acids and substituted dicarboxylic acids from malonic ester.

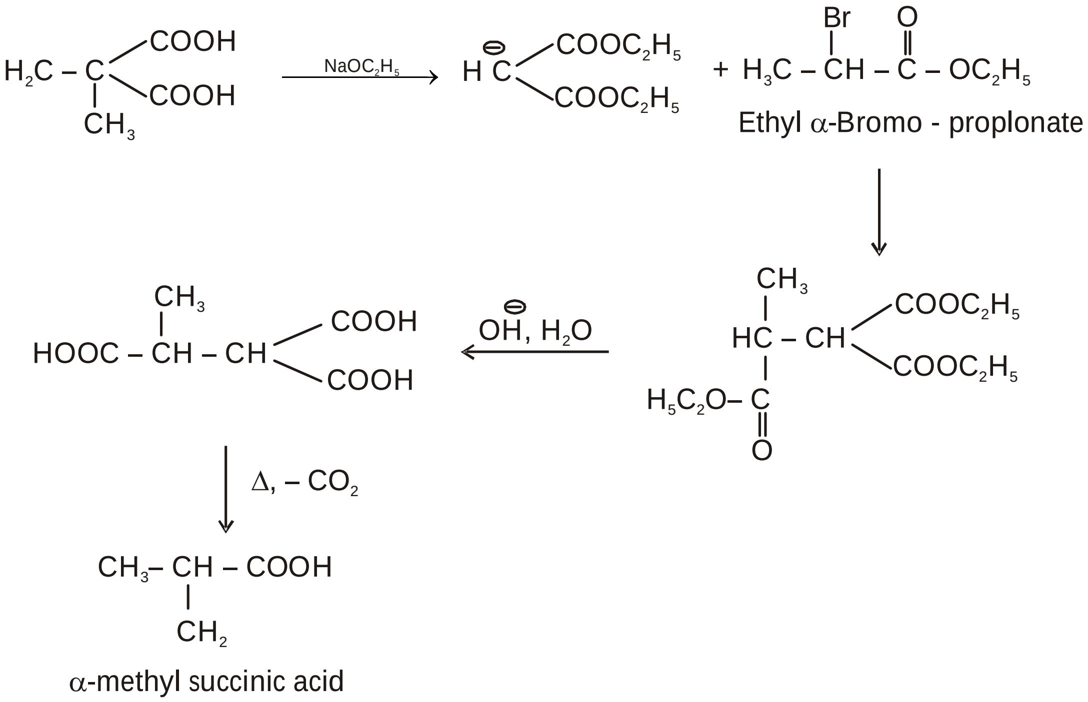
Ans :

(i) Preparation of substituted monocarboxylic acids :





(ii) Preparation of substituted dicarboxylic acid



S4-G-3: COLLOIDS AND SURFACE CHMISTRY

Q14. Define Colloids

Ans :

Colloids

Particles which are bigger than molecules but so smaller than suspension particles that they can not be seen under a most powerful microscope. Such particles are said to belong to the colloidal state and when suspended in a liquid, are referred to as colloidal solutions.

Q15. How are the Colloids classified? Give examples.

Ans :

Classification of Colloids

The colloidal systems with solid as dispersed phase and liquid as dispersion medium are known as sols. If the dispersion medium of colloidal system is gas, the system is known as aerosol. When the liquid medium is water, the system is known as hydrosol or aquasol; while if it is alcohol, benzene or any other organic liquid, the system is refferred to as an alcosol, benzosol.

Colloids may be of two types, viz., lyophilic or reversible and lyophobic or irreverible colloids. If water is the dispersion medium, the terms used are hydrophilic and hydrophobic.

1. **Lyophilic Colloids**

   A colloidal system obtained readily on simple warming or shaking the substance with a suitable solvent is known as lyophilic colloid (lyo-liquid ; philic-love) ; **Eg.** gelatin, starch, proteins, gum and rubber. Lyophilic colloids are also known as reversible colloids since on evaporating the dispersion medium (e.g., water), the residue can again be easily reconverted into colloidal state simply by addition of the liquid, i.e., water. These sols are quite stable and cannot be easily precipitated.

2. **Lyophobic Colloids**

   Colloids formed with difficulty are termed as lyophobic colloids (lyo liquid, phobic-hate) ; These colloids are formed by substance like As_2S_3, Fe $(OH)_3$, gold and other metals which are sparingly soluble and thus their molecules do not pass readily into colloidal state. Lyophobic colloids are known as irreversible colloids since the residue (obtained by evaporating the dispersion medium) cannot readily be reconverted into sol by ordinary means. These sols are readily precipitated (or coagulated) and hence are not stable.

Q16. Write the preparation of Colloids.

(OR)

Describe the different methods used for the preparation of Colloids. Give examples

Ans :

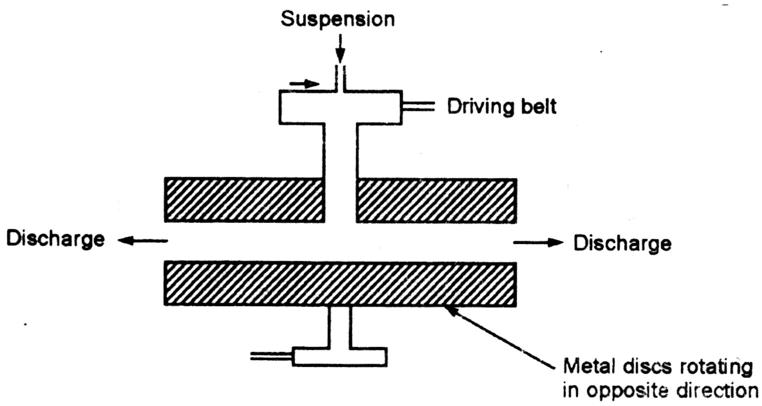
Preparation of Colloids

Colloidal solution of lyophilic colloids can be prepared readily by simply treating the substance with the dispersion medium. On the other hand, preparation of colloidal solution of lyophobic colloids requires special methods which are grouped under the two headings, viz. dispersion methods and condensation methods.

(A) Dispersion methods

In these methods the large particles are broken to smaller particles of colloidal size. The important dispersion methods are discussed below.

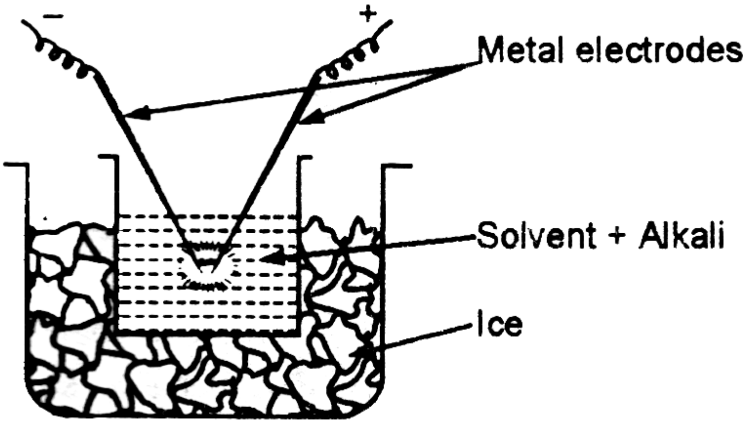
1. **By mechanical disintegration :** The substance is finely ground and agitated with the dispersion medium to get a suspension. This suspension is then fed between two steel discs having a very small clearance between them (colloids mills) and rotated in opposite directions at a very high speed (7000 revolutions per minute).



The suspension particles are turn off to colloidal dimensions

2. **By Bredig's arc method (electro-dispersion) :** If an electric arc is struck between two electrodes of a metal, like gold, silver, platinum or copper, in water having traces of an alkali, the metal is found to be converted into colloidal solution of a reasonable concentration

   By the heat of the spark the metal first changes into vapours which then condenss in cold water to give aggregates of colloidal range. Alkali acts as a stabliser. The coarser particles formed are filtered off.



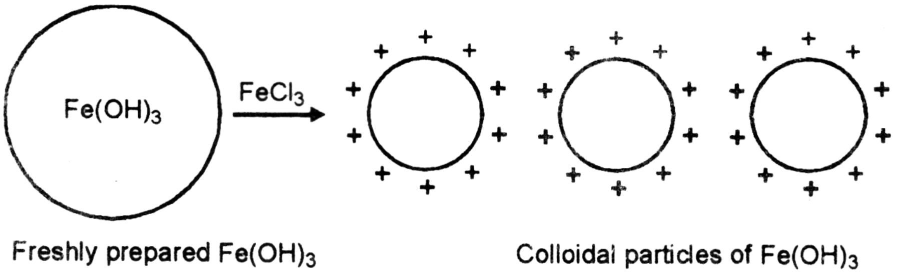
3. **Peptisation :** The precipitates of certain substances have already colloidal dimensions, but cannot be suspended in water or other dispersing medium for lack of affinity between the two. The addition of a stabilizer like sugar, gum or an electrolyte helps in stabilizing the suspension. This process of passing of a precipitate into colloidal particles by adding suitable electrolyte is known as peptisation and the stabilizing agent (or electrolyte) as peptizing agent.

   (i) Freshly prepared ferric hydroxide can be converted into colloidal state by shaking it with water containing Fe^{3+} or OH^- ions, viz, $FeCl_3$ or NH_4OH) respectively.

   (ii) A stable sol of stannic oxide is obtained by adding a small amount of dilute hydrochloric acid to stannic oxide precipitates.

   (iii) Similarly, a colloidal solution of $Al(OH)_3$ and AgCl are obtained by treating the corresponding freshly prepared precipitate with very dilute HC1 and $AgN0_3$ or KCl respectively.

   The electrolyte is added to a freshly precipitated substance, the particles of the precipitate preferentially adsorb one particular type of ions of the electrolyte and get dispersed due to electronic repulsions. This gives particles of colloidal size.



(B) Condensation or aggregation methods

In these methods, molecules condense or aggregate together to the particles of colloidal size. These methods may be physical or chemical. Among the following condensation methods the first three are physical others are chemical methods.

(i) **By excessive cooling :** When a solution of water in an organic solvent like chloroform or either is freezed - a colloidal solution of ice is obtained. Actually, the molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

(ii) **By exchange of solvent :** Colloidal solutions of substances which are insoluble in water but soluble in alcohol (e.g., phenolphthalein, sulphur and phosphorus) are obtained by pouring a small amount of their alcoholic solution to excess of water. However, such sols are usually unstable some stabilizer is also added.

(iii) **By passing vapour of an element into a liquid** : When vapour of mercury or sulphur are passed into water having a trace of stabilizing agent like ammonium citrate the colloidal solution is obtained.

(iv) **Chemical methods :** All chemical changes giving rise to insoluble products can be used for the formation of sol, provided a suitable stabilizer is present. The important chemical reactions used for the preparation of colloidal solutions are given below.

(a) **By oxidation :** A colloidal solution of sulphur can be obtained by bubbling oxygen (or any other oxidising agent, like $HN0_3$, Br_2, etc.) through a solution of hydrogen sulphide in water.

$$2H_2S + O_2 \text{ (or other oxidising agent)} \rightarrow 2H_2O + 2S$$

(b) **By reduction :** A number of metals, such as silver, gold and platinum, have been obtained in colloidal state by treating the aqueous solution of their salts with a suitable reducing agent, such as formaldehyde, phenylhydrazine, hydrogen peroxide, stannous chloride, etc.

$$2AuCl_3 + 3SnCl_2 \rightarrow 3SnCl_4 + 2Au$$

Gold sol

(c) **By hydrolysis :** Many salt solutions are rapidly hydrolysed by boiling dilute solutions of their salts. For example, ferric hydroxide and aluminium hydroxide sols are obtained by boiling solutions of the corresponding chlorides.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

Similarly, silicic acid sol is obtained by the hydrolysis of sodium silicate.

(d) **By double decomposition :** A sol of arsenic sulphide is obtained by passing hydrogen sulphide through a cold solution of arsenious oxide in water.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

Q17. Write the difference between lyophillic and lyophobic colloids.

Ans : **(Imp.)**

Difference between Lyophilic and Lyophobic Sols

Sl No:	Property	Lyophilic sols	Lyophobic sols
1	Reversibility	These are reversible	These are irreversible
2	Visibility	The particles cannot be readily detected even under ultra-microscope	The particles can be readily detected under ultramicroscopie
3	Surface tension	Surface tension is usually lover than that of the dispersing medium	Surface tension is of the same order as that of the dispersion medium
4	Viscosity	Viscosity is much higher than that of the dispersing medium	Viscosity range is about the same as that of the dispersion medium
5	Action electrolytes	Much large quantities of electrolytes are required to cause precipitation (Coagulation)	Addition of small quantities of electrolytes causes precipitation
6	Influence of electric field	The particles may or may not migrate under the influence of an electric field	The particles migrate either to cathode or to anode under the influence of an electric field
7	Hydration	Owing to the presence of a number of polar group in the molecules are appreciation	The particles are not hydrated to an appreciable extent

Q18. Write about protective colloids, gold number and Hardy – Schulze law.

Ans : **(Imp.)**

Protective Colloids

The extra stability of lyophilic colloids imparts them the property of protecting lyophobic colloids from precipitation by electrolytes. When a lyophoilic sol is added to a lyophobic sol, the former particles provide envelopes around the latter particles and thus protect the latter from the action of electrolytes. Lyophilic colloids used purposes are known as protective colloids. Thus the addition of gelation (lyophilic colloid) to a gold sol (lyophobic sol) protect by the action of limited amount of sodium chloride.

Gold Number ?

The gold number as the weight in milligrams of a protective colloid which checks the coagulation of 10 ml of a given gold solution on adding 1 ml of a 10% solution of sodium chloride. Thus smaller the gold number of a lyophilic colloid, greater is its protective power.

Hardy – Schulze law

When excess of an electrolyte is added the colloidal particle are precipitated. The colloidal particles take up ions carrying charge opposite to that present on themselves. This causes neutralization leading to their coagulation. The ion responsible for neuturalization of charge on the particles is called the flocculating ion. The greater the valency of the flocculating ion added the greater is the power to cause precipitation. This is known as Hardy Schulze rule.

Flocculating power of Na^+, Ba^{2+} and Al^{3+} in the order $Al^{3+} > Ba^{2+} > Na^+$

Q19. What is meant by electrophoresis?

OR

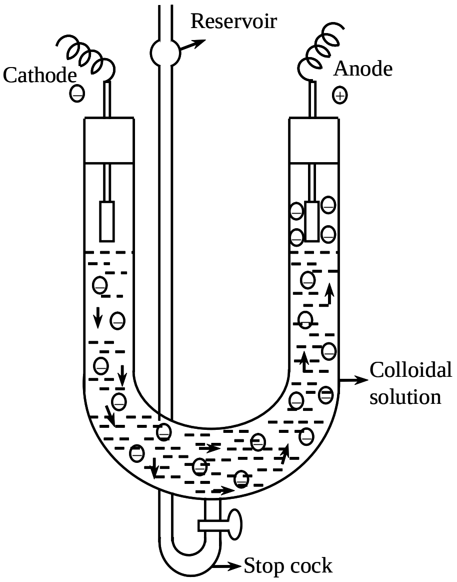
Explain the electrical property of colloids.

Ans : **(Imp.)**

Electrophoresis

When electric potential is applied across two platinum electrodes dipping in a choroidal solution. The colloidal particles move towards one or the other electrode. This movement of colloidal particles under and applied electric field is called electrophoresis.

OR



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

The apparatus consists of a ‘v’ tube provided with a stop cock through it is connected to a funnel shaped reservoir. A small amount of water is first taken in “U” tube and then a rearisity quantity of colloidal solution is placed in the reservior. The stopcock is slightly opened and the reservoir is gradually raised to introduce the colloidal solution into the u-tube. The water is displaced upwards producing a sharp boundary line in each arm. The platinum electrodes are fitted in the water layer and a voltage of 50-200 volts applied. The movement of the particles (or) be observed towards the electrodes by seeing the position of boundary. When the colloidal particles are negatively charged, the boundary moves down in the cathodic arm and moves upwards in the anodic arm showing that particles move towards anode.

Q20. What are emulsions. Give examples.

Ans : **(Imp.)**

Emulsions

Emulsions are colloidal systems in which the dispersed as well as dispersion phase is normally liquid. The two common examples are (i) milk which consists of particles of liquid fat dispersed in water, and (ii) cod-liver oil is which particles of water are dispersed in oil

In emulsion, the particles of dispersed phase are generally bigger than those in sols and are sometimes visible under the microscope. Emulsion particles carry a negative charge and are sensitive to the addition of electrolytes. They show Tyndall effect and Brownian movement. In most of emulsions, the two liquid phases are oil and water and thus emulsions, may be of following two types

(i) Oil-in-water emulsions

In these emulsions, oil is the dispersed phase and water is the dispersion medium. Milk and vanishing cream are the two important examples of this type of emulsion

(ii) Water-in-oil emulsion

In these emulsions, water is the dispersed phase and oil is the dispersion medium. Butter and cold cream are the common examples

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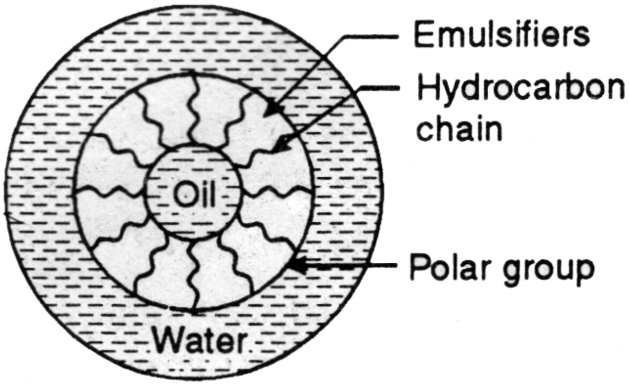
Q21. Write the preparation of emulsifiers.

Ans :

Emulsifiers

When two immiscible liquids, viz. oil and water are shaken together vigorously, an emulsion consisting of small globules of oil suspended in water is obtained.

This emulsion is stable only for a short period and on standing, the two constituent liquids soon separate, the oil globules rise to the top and form a separate oil phase. In order to get stable emulsions of high concentration, it is necessary to add another substance, known as emulsifier or emulsifying agent, in a small amount.



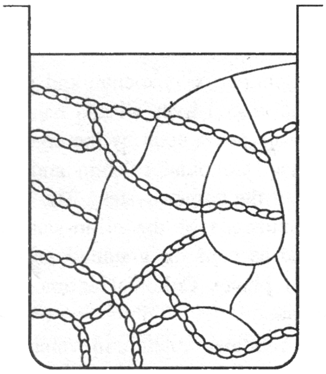
The emulsifiers are usually long chain groups such as soaps, long chain sulphonic acids and alkyl sulphates. These emulsifying agents decrease the interfacial tension between the two liquids and thus facilitate mixing of the two liquids. Emulsifier lowers the interfacial tensions, it gets concentrated at the interface and forms thin film over the surface of the droplets which helps to prevent their coalscence.

Q22. What are gels and Classify the gels?

Ans :

Gels

Colloidal systems containing a liquid dispersed in solid are termed gels. For example, when a warm sol of gelatin is cooled, it sets to a semi-solid mass which is gel. The process of gel formation is known as gelation. Common examples of gels are curd (gel of water in casein), table jelly (gel of water in gelatin) and solid alcohol (get of alcohol in calcium acetate). Soap, boot polishes, animal tissues and a number of food stuffs have a gel structure.



Gelation may be thought of a partial coagulation of a sol. The coagulating sol particles first unite to form long threat-like chanins. These chains are then inter-locked to form a solid framework. The liquid (dispersion medium) gets trapped in the cavities of this frame work and is possibly held by capillary action.

Classification of the gels

Gels may be of two types

a) **Elastic gels**

These posses the property of elasticity. They change their shape of applying force and return to original shape when the force is removed. Examples are gelatin, starch and soaps. The linkage between particles is due to electrical is due to electrical attraction and are not rigid.

b) **Non-elastic gels**

These are rigid and prepared by appropriate chemical reaction. For example, silica gel is produced by adding concentrated HCl to sodium silicate solution of the correct concentration, resulting silicic acid which poelisesses to form silica gel. It has a network linked by covalent bonds which give a strong and rigid structure.

Q23. Write the properties of gels.

Ans :

Properties of Gels

(i) **Hydration**

A completely dehydrated elastic gel can be regenerated by addition of water. But once a nonelastic gel is freed from moisture addition of water will not bring about gelation.

(ii) Swelling

Partially dehydrated elastic gels imbibe water when immersed in the solvent. This increases the volume of the gel and hence the process is called swelling

(iii) Syneresis or Weeping

On standing a gel may shrink and lose the liquid held by it. This is termed as syneresis or weeping

(iv) Thixotropy

Some gels liquify on shaking and reset when allowed to stand. This reversible sol gel transformation is referred to as thixotropy. This phenomenon is observed in marshy lands which soften on treating and reset on standing. This is due to the presence of bentonite clay present in such soils.

Q24. Write natural and technical applications of Colloids.

Ans :

Importance and Applications of Colloids and Emulsions

Colloids play very important role in our everyday life as well as in industry, agriculture, medicines and biology. Some of the important applications are discussed below

1. Colloids in nature

Several important materials are colloidal in nature

(a) **Foodstuffs :** Many of our foodstuffs are colloidal in nature. For example, milk is an emulsion of fat dispersed in water and stabilized by casein which itself is a lyophilic colloidal an being a protein, is a nutrient, of a great value, other food stuffs colloidal in nature are eggs, fruits, jellies, whipped cream, salad dressings etc.

(b) **Medicines :** A great number of medicinal and pharmaceutical preparations are emulsion, e.g., emulsions of cod liver oil and halibut liver oil. Colloidal calcium and gold are administered by injections to raise the vitality of the human system. The disinfectant such as phenyl, dettol and lysing produce emulsions of the oil-in-water type when poured into water. Colloidal silver is used as cure for granulations.

(c) **Soils :** Good soils are colloidal in nature in which human acts as a protective colloid

(d) **Rain :** Clouds are tiny droplets of water dispersed in air. Rain is caused by the aggregation of these minute particles to form bigger drops of water which fall down under the action of gravity

(e) **Blue colour of the sky :** The blue colour of the sky is due to scattering of light by the colloidal particles of dust in air

(f) **Blood :** Blood is a colloidal solution of an albuminoid substance. The colloidal nature of blood explains why bleeding stops by applying a feeric chloride solution to the wound. Ferric chloride solution causes coagulation of blood to form a clot which stops further bleeding.

2 Purification of water

The impure water clay particles and bacteria. The presence of clay particles is responsible for the turbidity in water. The addition of potash alum or aluminium sulphate furnishes the trivalent aluminium ions which cause the coagulation of the clay particles, along with bacteria (if any) settle down leaving water in clear state.

3. Sewage disposal

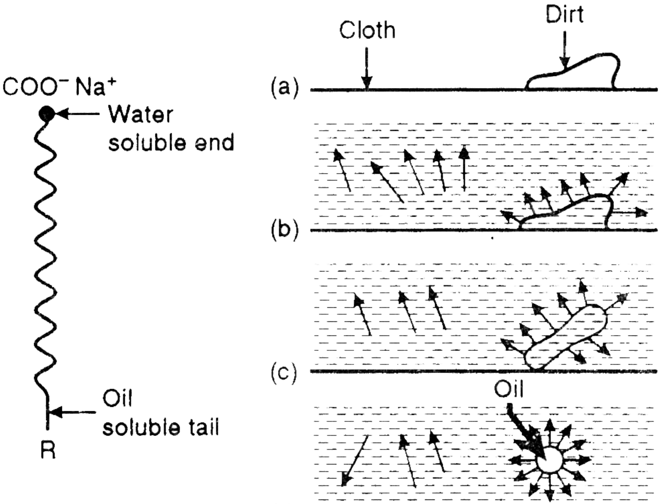
Sewage water contains particles of dirt, rubbish, mud etc. which are of colloidal size and carry electric charge and, therefore, do not settle down easily. These particles can be removed by the process of cataphoresis in which sewage water is passed through a tunnel fitted with metallic electrodes, maintained at high potential difference. The particles migrate to the oppositely charged electrodes, get neutralized and settle down (coagulated). The deposited matter (rubbish matter) is used as a manure and the clear water is used for irrigation purpose.

4. Cleansing action of soap

The dirt sticks to the clothes with the help of greasy or oily material grease is not readily wettred by water, it is difficult to clean the clothes by water alone. Soap solution removes the dirt by adsorption or emulgjfying the greasy matter sticking to cloth.

A soap molecule has two dissimilar ends. viz. a polar end comprising the salt end -COONa and a end comprising the long hydrocarbon chain. The polar end is water-soluble (hydrophillic) while the non-polar end is oil soluble (lyophilic or lipophilic).

The dirt particles are held together on the cloth by some greasy material, say oil (Fig. 15.20a). When soap and dirt are brought in contact with each other in the presence of water, the non-polar end of the soap molecule dissolves in the oil present in dirt (Fig. 15.20 b), begin to lift it up (Figure), surround the oil Fig. 15.20 d) and hold it in suspension so that it can be washed away.



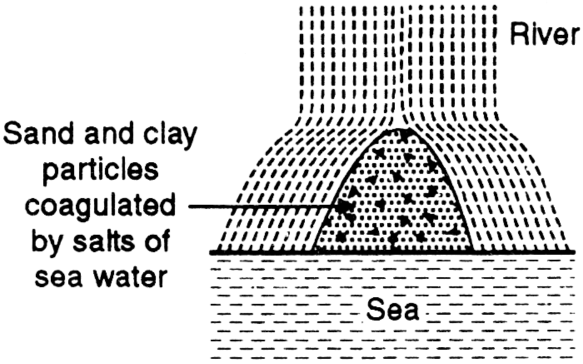
5. Rubber plating and chrome tanning

Several industrial processes such as rubber plating, chrome tanning, dyeing, lubrication, etc. are of colloidal nature.) The first two processes are, In rubber plating, the negatively charged particles of rubber (latex) are made deposit on the wires or handles of various tools (in order to insulate them) by means of electrophoresis. The article on which rubber is to be deposited is made anode.

In tanning, the positively charged colloidal particles of hides and leather are coagulated by impregnating them in negatively charged tanning materials (present in the barks of trees). Among the tanning agents, chromium salts are most commonly used for the coagulation of the hide material and the process is called *chrome tanning.* The rate of chrome tanning can be increased by electrophoresis.

6. Delta formation

When river water containing charged clay and sand particles meet the sea water containing sodium chloride, the charged clay and sand particles lose their charge and settle down at the point of contact. Thus the level of river bed rises, water adopts a different route and delta is formed in due course of time.



7. Smoke screens

Smoke screens are used in warfare for the purpose of concealment. These screens consist of very fine particles of titanium oxide dispersed in air. These are dropped from aeroplanes and since titanium oxide is very heavy, the smoke screen drops down rapidly as a certain of dazzling whiteness.

Q25. Write the properties of Colloids.

Ans :

Properties Of Colloidal System

The important properties of colloidal systems are described below

1. Heterogeneous Character

Unlike true solutions, colloidal systems are heterogeneous in nature. They consist of two phases, viz. the dispersed phase and the dispersion phase.

2. Non-setting

Colloidal solutions are stable systems

3. Filtrability

Colloidal particles readily pass through ordinary filter papers. However, they can be retained by special filters known as ultrafilters (parchment paper or animal membrane)

4. Visibility

Very small size the colloidal particles are not visible even under a most powerful microscope.

5. Colour

A silver sol passes from brown to black and finally spangles. Diluted milk gives a bluish tinge to reflected light and reddish tinge in transmitted light.

6. Colligative properties

The value of osmotic pressure, lowering of vapour pressure, despression in freezing point and elecation of boiling point depends upon the number of solute particles present in a given weight of the solvent. Further colloidal particles are not simple molecules but are physical aggregation of molecules. Thus for a given mass of sol, the number of particles will be very small as compared to the number of particles in true solution

The colloidal system gives very low osmotic pressure and show very small freezing point depression or boiling point elecation.

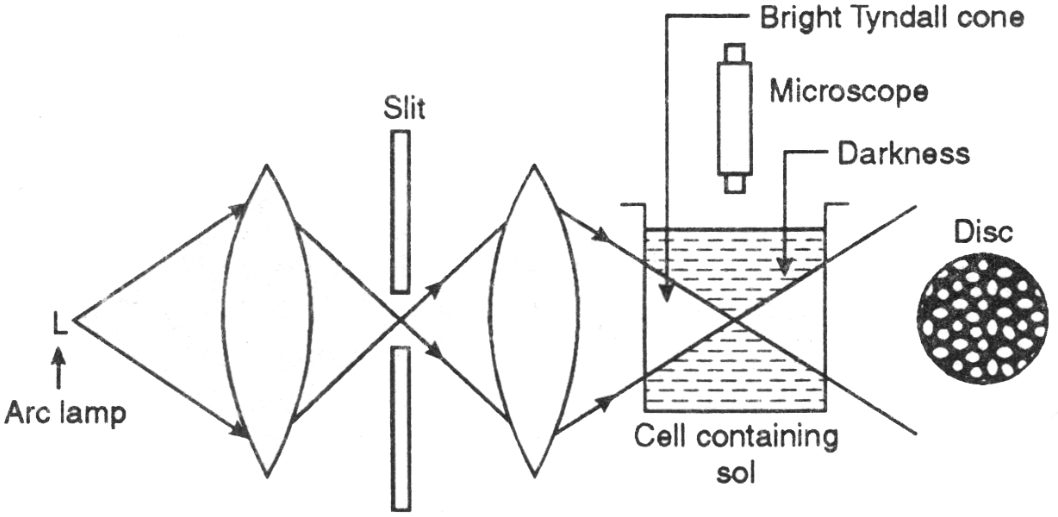
7. Tyndall effect (Optical Property)

Tyndall, in 1869 observed that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in path. When the same beam of light is passed through a colloidal suspension it becomes visible as a bright streak. This phenomenon is called Tyndall effect and the illuminated path (Streak of light) is known as Tyndall cone. The Tyndall effect is owing to the scattering of light form the surface of colloidal particles.

The appearance of dust particle in a semi-darkened room when a sun beam enters or when a light is thrown from a projector in cinema hall, are the well known examples of Tyndall effect. the dust particles are large enough to scatter light which renders the path of light visible.

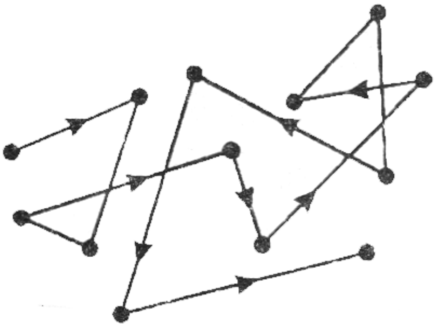
Ultra-microscope

A strong beam of light from an arc lamp or other powerful s condensed by a system of lenses and a knife edged slit and passed through the colloidal solution placed in a cell. The scattered beam can easily be viewed with the help of a microscope placed at right angles to the beam. In this way, the colloidal particles, which are too small to be seen under an ordinary microscope, can be detected as *bright spots* or *discs of light* moving irregularly.



8. Brownian movement (Kinetic Property)

Robert Brown, an English botanist, in 1827, observed that pollen grains in aqueous suspension were in constant motion. This Brownian movement is due to the bombardment of colloidal particles by the molecules of the dispersion medium (Figure b) which are in constant motion like molecules in a gas. The colloidal particles acquire nearly the same kinetic energy as possessed by the molecules of the dispersion medium. Now since the colloidal particles are considerably heavier than the molecules of the dispersion medium, their movement is considerably slower than that of the medium molecules and hence can be observed under the ultramicroscope.



Electrical property

The most important property of colloidal particles is that these are electrically charged. All the particles of a colloidal system carry the same charge while the dispersion medium has an equal but opposite charge with the result the system as a whole is electically neutral. The presence of equal and similar charge on colloidal particles is mainly responsible in giving stability to the system. The colloidal particles, owing to the similar nature of the charge, repel each other and do not combine to form bigger particles and thus the sol is stable and particles do not settle down.

Q26. Define adsorption and adsorption.

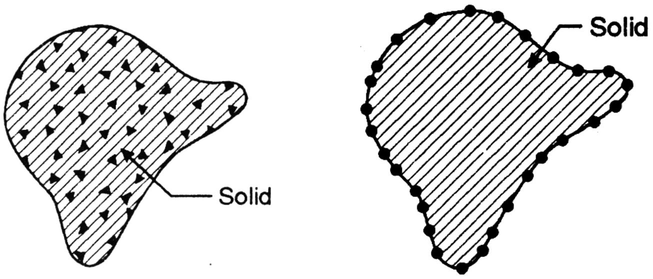
Ans :

This phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid is known as adsorption. The substrate (solid substance) on which adsorption takes place is called the adsorbent; while the adsorbed material (a gas or a liquid) is called adsorbate.

The term adsorption refers to the attraction and retention of the molecules of a substance only on the surface of the solid (Figure (a)) while the term absorption refers passing of the substance through the surface into the bulk of the solid (Figure (b)). Two examples of absorption are given below for clarification,

(i) Ink is absorbed by the chalk.

(ii) When a few drops of water are added to a lump of sugar, water is soaked by the entire mass.



(a) Adsorption (b) Absorption

Fig.: Distinction between adsorption and absorption

Q27. Write the types of adsorptions and give examples.

Ans :

Types of Adsorption

Adsorption of gases on solids may be of two types depending upon the type of force operative in adsorption processes.

1. **Physical adsorption or vander Waal's adsorption:** When a gas is held (adsorbed) on the surface of a solid (adsorbent) by weak vander Waal's forces, the phenomenon is known as physical adsorption since no chemical bond is set up between the adsorbate (gas) and adsorbent (solid).

   All gases are adsorbed on all solids to some extent.

2. **Chemical adsorption or Chemisorption:** When a gas is held (adsorbed) onto the surface of a solid by forces similar to those of a chemical bond. The adsorption is known as chemical adsorption. Thus, chemisorption leads to the formation of the so called a surface compound. Thus chemisorption takes place only if the gas to be adsorbed is capable of forming a chemical bond with the surface atoms (adsorbent).

   For example, hydrogen is adsorbed on the transition metals with unpaired d-electrons leading hydride formation. Similarly, oxygen is adsorbed on the metals with the formation of oxide.

Q28. What are the differences between physical adsorption and chemsorption.

Ans :

S.No.	Physical adsorption	S.No.	Chemisorption
1.	It involves physical force, i.e., weak vander Waal's forces.	1.	It involves transfer of electrons between gas and solids, i.e., the forces operating are similar to those in chemical bond.
2.	Adsorption is multilayer.	2.	Adsorption is a only in the upper layer.
3.	Heat of adsorption is low.	3.	Heat of adsorption is high.
4.	The process is reversible, i.e., desoption of the gas occurs by decreasing the pressure of increasing the temperature.	4.	The process is irreversible efforts to free the adsoorbed gas give some definite chemical compound formed between gas adsorption.
5.	It does not show specificity.	5.	It is a highly specific.
6.	More easily liquefiable and more soluble gas is adsorbed more readily.	6.	Gases having potentiality of compound formation with the adsorbent are chemisorbed.
7.	It decreases with increases in temperature.	7.	It increases with increase in temperature.

Table : Distinction between physical adsorption and chemisorption

Q29. What is Freundlich adsorption isotherm.

Ans :

Adsorption Isotherm

The quantity of a gas adsorbed by a given amount of adsorbed depends upon both temperature and pressure. At constant temperture, adsorption of a gas on a solid surface (adsorbent) increases with increae in pressure of the gas. This relation between the amount adsorbed by an adsorbent and the pressure (or concentration) of the gas (adsorbate) at a constant temperature is called the adsorption isotherm.

1. **Freundlich Adsorption Isotherm :** Freundlich gave an empirical relationship betweent he quantity of gas adsobed by a given amount of solid adsorbent surface and pressure of the gas at a particular temperature. It states that

$$\frac{x}{m} = kp^n \quad \text{(Freundlich Adsorption Isotherm)}$$

where x is the weight of the gas adsorbed by m gm of the adsorbent at a pressure p ; thus x/m represents the amount of gas adsorbed per gm (unit mass) of the adsorbent, k and n are constants at a particualr temperature and for particular adsorbent and adsorbate (gas); n is always less than one indicating that the amount of the gas adsorbed does not increase as rapidly as the pressure.

$$\log \frac{x}{m} = \log k + n \log p$$

Thus the Freundlich isotherm can be tested by plotting log x/m against log p. The plot must be a straight line.

This isotherm is also used for adsorption of the solutes from solution and has been found to work better with this type of adsorption than with gases. The pressure in the expresson is replaced by equilibrium concentration (C) of the solute i.e.,

$$\frac{x}{m} = k\,C^n$$

$$\text{or} \quad \log \frac{x}{m} = \log k + n \log C$$

k and n are empirical constants depending on the system and the temperature.

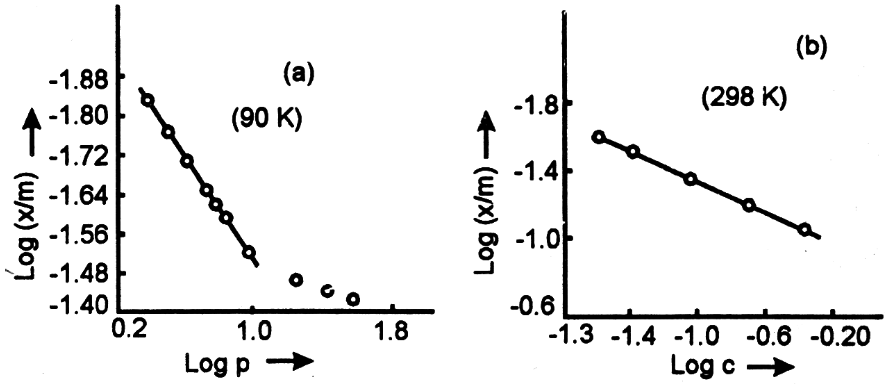


Fig.: Adsorption isotherms (a) Nitrogen on mica at 90 K (b) Acetic acid on charcoal at 298 K.

Q30. Describe briefly Langmuir's theory of adsorption and its applications.

Ans :

Langmuir Adorption Isotherm

(i) Adsorption takes place on the surface of solid only fill whole of surface is completely covered with a unimolecular layer adsorbed gas.

(ii) Adsorption consists of two opposing processes, namely (a) condensation of the gas molecules on the solid surface and (b) evaporation (desorption) of the gas molecules from the surface back into the gaseous phase.

(iii) The rate of condensation depends upon the uncovered (bare) surface of the adsorbent available for condensation. Naturally at start when whole of the surface is uncovered the rate of condensation is very high and as the surface is covered more and more the rate of evaporation depends upon the covered surface and hence increases as more and more of the surface is covered. Ultimately an equilibrium will set up at a stage when the rate of condensation becomes equal to the rate of evaporation (adsorption equilibrium).

(iv) The rate of condensation also depends upon the pressure of the gas since according to kinetic theory of gases, the number of molecules striking per unit area is proportional to the pressure.

Derivation of Langmuir Isotherm

The fraction of the surface covered by adorbed molecules = q

$\therefore$ the fraction of the surface uncovered = 1 – q

the pressure of the gas = p

The rate of adsorption is proportional tot he pressure (p) of the gas as well as uncovered surface $(1 - \theta)$ of the adsorpbent available for adsorption.

$$\text{Rate of adsorption} \propto p(1 - \theta)$$
$$= k_1P(1 - \theta)$$

where K_1 is a proportionality constant.

$$\text{Rate of desorption (evaporation)} \propto \theta = K_2\,\theta$$

where K_2 is another proportionality constant

At equilibrium,

Rate of adsorption = Rate of desorption

$$K_1p(1 - \theta) = K_2\theta$$
$$K_1p - K_2p\theta = K_2\theta$$
$$\theta\,(K_2 + K_1p) = K_1p$$
$$\theta = \frac{K_1p}{(K_2 + K_1p)}$$
$$\theta = \frac{\frac{K_1}{K_2p}}{1 + \frac{K_1}{K_2p}} = \frac{ap}{1 + ap}$$

where $\frac{K_1}{K_2}$ = a which is another constant.

the gas molecules are assumed to form a layer one molecule thick on the surface, the amount of gas adsorbed per unit area or per unit mass of adsorbent must be proportional to the fraction of the surface covered, i.e.,

$$\frac{x}{m} \propto \theta; \frac{x}{m} = K_3\theta$$

where x is the mass of the gs adsorbed on m gram of the adsorbent and K_3 is the proportionality constant.

Substituting the value of θ from equation in the above equation, we get

$$\frac{x}{m} = K_3 \frac{ap}{1+ap}$$

$$\frac{x}{m} = \frac{bp}{1+ap}$$

where b is the new constant for the product K_3a.

Equation is the Lagmuir adsorption isotherm. The values of the constant a and b depend upon the nature of the gas (adsorbate), nature of the solid adsorbent and the temperature. Their values can be determined from the experiment data.

Verification of the validity of Langmuir is adsorption equaiton. At any one temperature, the Langmuir's isotherm can be verfified by first dividing the equation by p on both sides to get

$$\frac{x/m}{p} = \frac{b}{1+ap}$$

and then taking the reciprocal to get

$$\frac{p}{x/m} = \frac{1}{b} + \frac{a}{b}p$$

since a and b are constants, a plot of $\frac{p}{x/m}$ against p should gie a straight line with slope equal to a/b and intercept on they y axis equal to 1/b.

For the adsorption of nitrogen on mica at 90 K.

Superiority of Langmuir's Adsorption Isotherm to the

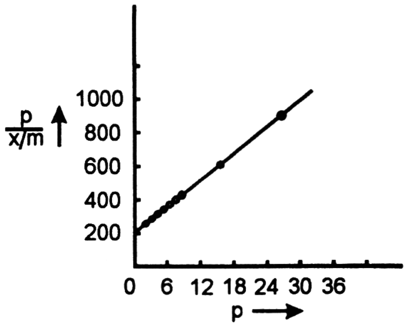


Fig.: Langmuir adsorption isotherm for adsorption of N_2 on mica at 90K

Limitation of Langmuir theory. Langmuir's theory of unimolecular adsorption is valid only at comparatively low pressure and high temperatures. As the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modem concept of multilayer adsorption.

Short Question and Answers

1. Write the Limitations of VBT theory.

Ans :

(i) The valence bond theory provides only a qualitative explanation of various metallic properties like electrical conductance, thermal conductance, high degree of malleability and ductility, high elasticity and high density.

(ii) It fails to do so on a quantitative scale.

(iii) The theory also does not explain metallic character in the liquid state or in solution.

2. Give the Limitations of free electron theory.

Ans :

1. It does not clearly explained semi- conductance.
2. It does not explain the specific heats of metals.

3. Write about n-type and p-type semiconductors.

Ans :

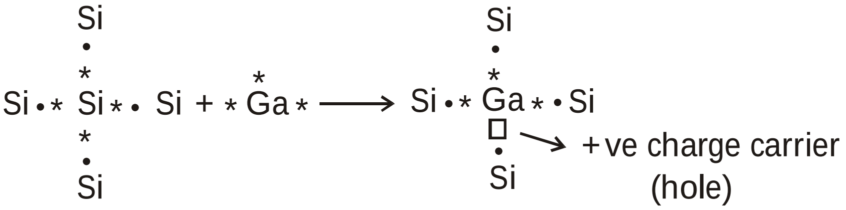
(i) n-type semiconductors

This type of semiconductor is produced due to metal excess defect and by adding trace amounts of group 15 elements like P, As, Sb to the group 14 elements like 'Si' and 'Ge'. 'Si' and 'Ge' have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. But 15 group elements P, As or Sb contain five valence electrons, they occupy some of the lattice sites in 'Si' or 'Ge' crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring 'Si' atoms. The fifth e^- extra and become delocalized. These delocalized e^-s increase the conductivity.

Since, no. of negatively charge carriers are more compared to positively charged carriers are called n-type Semiconductors.

(ii) p-type semiconductors

Si /Ge are doped with Group (III) elements like B/Al/Ga, which possess 3 valence electrons.

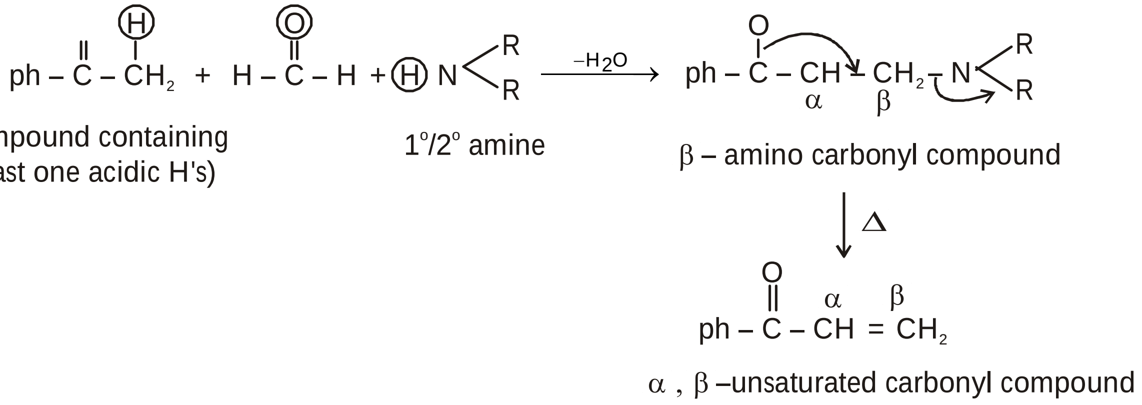


Since no. of positively charged carriers are more compared to negatively charged carriers called p-type semiconductors.

4. Write the mannich reaction.

Ans :

Mannich reaction :



$$\text{ph}-\overset{\|}{C}-CH_2 + H-\overset{\overset{O}{\|}}{C}-H + HN\begin{smallmatrix}R\\R\end{smallmatrix} \xrightarrow{-H_2O} \text{ph}-\overset{\overset{O}{|}}{C}-\underset{\alpha}{CH}-\underset{\beta}{CH_2}-N\begin{smallmatrix}R\\R\end{smallmatrix} \xrightarrow{\Delta} \text{ph}-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{CH}=\overset{\beta}{CH_2}$$

(Compound containing at least one acidic H's)

1°/2° amine

β – amino carbonyl compound

α , β –unsaturated carbonyl compound

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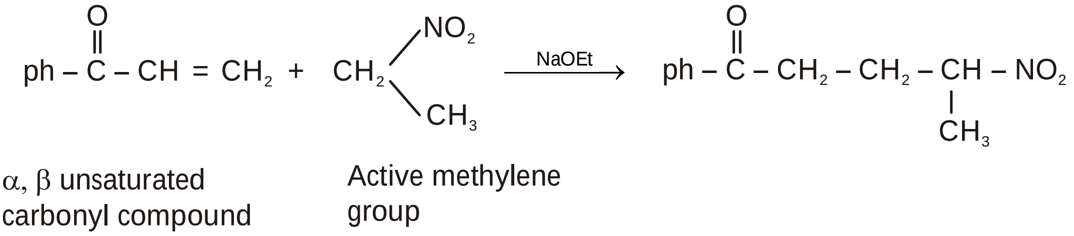
5. Write the Michel addition reaction.

Ans :



$$\text{ph}-\overset{\overset{O}{\|}}{C}-CH=CH_2 + CH_2\begin{smallmatrix}NO_2\\CH_3\end{smallmatrix} \xrightarrow{NaOEt} \text{ph}-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-NO_2$$

α, β unsaturated carbonyl compound

Active methylene group

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6. Write the Synthetic applications of Malonic ester.

Ans :

Malonic ester can be used in the preparation of substituted monocarboxylic acids and substituted dicarboxylic acids.

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7. What ate Lyophilic Colloids and Lyophobic Colloids?

Ans :

Lyophilic Colloids

A colloidal system obtained readily on simple warming or shaking the substance with a suitable solvent is known as lyophilic colloid (lyo-liquid ; philic-love) ; substances like gelatin, starch, proteins, gum and rubber form this type of colloids. Lyophilic colloids are also known as reversible colloids since on evaporating the dispersion medium (e.g., water), the residue can again be easily reconverted into colloidal state simply by addition of the liquid, i.e., water. These sols are quite stable and cannot be easily precipitated.

Lyophobic Colloids.

Colloids formed with difficulty are termed as lyophobic colloids (lyo liquid, phobic-hate) ; such colloids are formed by substance like As_2S_3, Fe $(OH)_3$, gold and other metals which are sparingly soluble and thus their molecules do not pass readily into colloidal state. Lyophobic colloids are known as irreversible colloids since the residue (obtained by evaporating the dispersion medium) cannot readily be reconverted into sol by ordinary means. These sols are readily precipitated (or coagulated) and hence are not stable.

8. What is meant by protective Colloids ?

Ans :

The extra stability of lyophilic colloids imparts them the property of protecting lyophobic colloids from precipitation by electrolytes. When a lyophoilic sol is added to a lyophobic sol, the former particles provide envelopes around the latter particles and thus protect the latter from the action of electrolytes. Lyophilic colloids used purposes are known as protective colloids. Thus the addition of gelation (lyophilic colloid) to a gold sol (lyophobic sol) protect by the action of limited amount of sodium chloride.

9. What is gold number ?

Ans :

The gold number as the weight in milligrams of a protective colloid which checks the coagulation of 10 ml of a given gold solution on adding 1 ml of a 10% solution of sodium chloride. Thus smaller the gold number of a lyophilic colloid, greater is its protective power.

10. State and explain Hardy – Schulze law.

Ans :

When excess of an electrolyte is added the colloidal particle are precipitated. The colloidal particles take up ions carrying charge opposite to that present on themselves. This causes neutralization leading to their coagulation. The ion responsible for naturalization of charge on the particles is called the flocculating ion. The greater the valency of the flocculating ion added the greater is the power to cause precipitation. This is known as Hardy Schulze rule.

Flocculating power of Na^+, Ba^{2+} and Al^{3+} in the order $Al^{3+} > Ba^{2+} > Na^+$

11. What are gels ?

Ans :

Gels

Colloidal systems containing a liquid dispersed in solid are termed gels. For example, when a warm sol of gelatin is cooled, it sets to a semi-solid mass which is gel. The process of gel formation is known as gelation. Common examples of gels are curd (gel of water in casein), table jelly (gel of water in gelatin) and solid alcohol (get of alcohol in calcium acetate). Soap, boot polishes, animal tissues and a number of food stuffs have a gel structure.

Gelation may be thought of a partial coagulation of a sol. The coagulating sol particles first unite to form long threat-like chanins. These chains are then inter-locked to form a solid framework. The liquid (dispersion medium) gets trapped in the cavities of this frame work and is possibly held by capillary action.

12. Classify the gels.

Ans :

Gels may be of two types

(a) Elastic gels

These posses the property of elasticity. They change their shape of applying force and return to original shape when the force is removed. Examples are gelatin, starch and soaps. The linkage between particles is due to electrical is due to electrical attraction and are not rigid.

(b) Non-elastic gels

These are rigid and prepared by appropriate chemical reaction. For example, silica gel is produced by adding concentrated HCl to sodium silicate solution of the correct concentration, resulting silicic acid which poelisesses to form silica gel. It has a network linked by covalent bonds which give a strong and rigid structure.

13. What is Thixotropy?

Ans :

Some gels liquify on shaking and reset when allowed to stand. This reversible sol gel transformation is referred to as thixotropy. This phenomenon is observed in marshy lands which soften on treating and reset on standing. This is due to the presence of bentonite clay present in such soils.

14. What is Tyndall effect?

Ans :

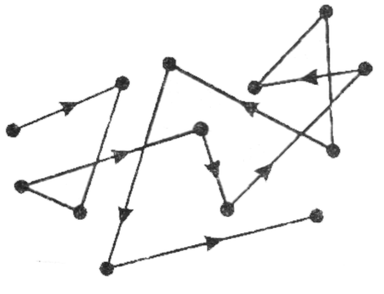
Tyndall, in 1869 observed that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in path. When the same beam of light is passed through a colloidal suspension it becomes visible as a bright streak. This phenomenon is called Tyndall effect and the illuminated path (Streak of light) is known as Tyndall cone. The Tyndall effect is owing to the scattering of light form the surface of colloidal particles.

The appearance of dust particle in a semi-darkened room when a sun beam enters or when a light is thrown from a projector in cinema hall, are the well known examples of Tyndall effect. the dust particles are large enough to scatter light which renders the path of light visible.

15. What is Brownian movement (Kinetic Property).

Ans :

Robert Brown, an English botanist, in 1827, observed that pollen grains in aqueous suspension were in constant motion. This Brownian movement is due to the bombardment of colloidal particles by the molecules of the dispersion medium (Figure b) which are in constant motion like molecules in a gas. The colloidal particles acquire nearly the same kinetic energy as possessed by the molecules of the dispersion medium. Now since the colloidal particles are considerably heavier than the molecules of the dispersion medium, their movement is considerably slower than that of the medium molecules and hence can be observed under the ultramicroscope.



Choose the Correct Answer

1. Which of the following theory can explain the metallic properties. [d]

   (a) Valence bond theory (b) Molecular orbital theory

   (c) Free electron theory (d) All the above

2. The addition of 15th group elements to pure Si or Ge produce _______. [b]

   (a) Super conductors (b) n-type semiconductors

   (c) p-type semiconductors (d) Insulators

3. The addition of 13th group elements to pure ‘Si’ or ‘Ge’ produces _______. [c]

   (a) n-type semiconductors (b) Super conductors

   (c) p-type semiconductors (d) Insulators

4. Which of the following compound is crotonic acid [b]

   (a) $HOOC - CH_2 - COOH$ (b) $H_3C - CH = CH - COOH$

   (c) $CH_3 - CH_2 - CH_2 - COOH$ (d) $HOOC - CH_2 - CH_2 - COOH$

5. Which of the following is a sygnthetic application of acetoacetic ester [c]

   (a) Synthesis of alcohols (b) Synthesis of aldehydes

   (c) Synthesis of ketones (d) Synthesis of esters

6. Which of the following is a synthetic application of malonic ester [a]

   (a) Synthesis of substituted carboxylic acids

   (b) Synthesis of aldehydes

   (c) Synthesis of ketones

   (d) Synthesis of alcohols

7. Knoevengeal condensation reaction is a _______. [c]

   (a) Electrophilic addition reaction (b) Electrophilic substitution

   (c) Nucleophilic addition reaction (d) Nucleophilic substitution

8. Valeric acid can be synthesised from _______ compound. [b]

(a) Ethyl aceto ester
(b) Malonic ester
(c) Malonic acid
(d) Crotonic acid

9. Difference between crystalloid and colloid is of [a]

(a) Particle size
(b) Chemical composition
(c) Inoic characters
(d) Solubility

10. The size of the colloidal particle is in between [c]

(a) $10^{-7} - 10^{-9}$ cm
(b) $10^{-9} - 10^{-11}$ cm
(c) $10^{-5} - 10^{-7}$ cm
(d) $10^{-2} - 10^{-3}$ cm

11. If liquid is dipersed in solid medium then this is called [d]

(a) Sol
(b) Emulsion
(c) Liquid aerosol
(d) gel

12. Which of the following forms a colloidal solution in water? [d]

(a) NaCl
(b) Glucose
(c) $Ba(NO_3)_2$
(d) Stasch

13. The number of phases present in colloidal solution [a]

(a) 2
(b) 4
(c) 3
(d) 1

14. Water loving colloids are called a [a]

(a) Hydrophilic
(b) Hydrophobic
(c) Lyophobic
(d) Irreversible

15. Colloids are perified by [c]

(a) Browninan motion
(b) Precipitation
(c) Dialysis
(d) Filtration

16. The kinetic activity of collodial particles in disperssion medium is known as [c]

(a) electro-osmosis (b) cataphoresis

(c) brownnian movement (d) electropharesis

17. The sky looks blue due to [d]

(a) Dispersion effect (b) Reflection

(c) Transmission (d) Scattering

18. Tyndall effect in colloidal solution is due to [b]

(a) Absorption of light (b) Scattering of light

(c) Reflection of light (d) Presence of electrically charged particles

19. What type of molecules form micelles? [ ]

(a) nonpolar molecales (b) Polar molecules

(c) Surfactant molecule (d) Satt of weak acid and weak base

20. Above CMC (critical micelle concentration) the surfactant molecules undergo [b]

(a) Dissociation (b) Aggregation

(c) Micelle formation (d) All of the

21. Micelles are used in [a]

(a) Detergents (b) Magnetic separation

(c) Petroleam recovery (d) All of these

22. During micelle formater [a]

(a) $\Delta H = + Ve, \Delta S = + ve$ (b) $\Delta H = - Ve, \Delta S = - Ve$

(c) $\Delta H = - Ve, \Delta S = + Ve$ (d) $\Delta H = + Ve \ \Delta S = - Ve$

23. A micelle formed during the cleansing action of soop is [a]

(a) a discrete partical of soap (b) aggregated particles of soap and dirt

(c) a discrete particle of dust (d) an aggregated partical of dust and water

24. An emulsified is a substance which [a]

(a) Statilises the emulsion (b) Homogenises the emulsion

(c) Coagulates the emuision (d) Acceterates the dispersion of liquid in liquid

25. Gold number is associated with [c]

(a) Electrophoresis (b) Purple of cassius

(c) Protective colloid (d) Amount of pure gold

26. Muddy water can be purified through coagalation using [b]

(a) Common salt (b) Alums

(c) Sand (d) Time

27. Tails of comets are visible due to [a]

(a) Tynd all effect (b) Reflection

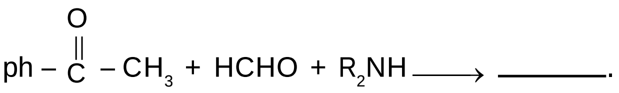
(c) Broanian movement (d) None of these

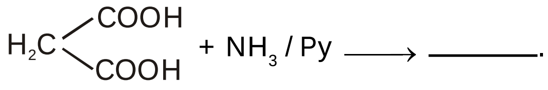
28. Silver iodide is used for producing artificial rain because AgI. [a]

(a) has crystal structure similar toice (b) is easy to spray at high attitudes

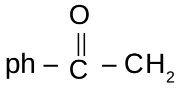
(c) is easy to synthesise (d) is soluble in water

Fill in the blanks

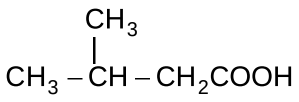
1. Band theory is also called as ________.
2. Free electron theory does not explain the ________ meta is
3. n-type and p-type semiconductors are belongs to ________ semiconductors
4. 

   $ph-\overset{\overset{O}{\|}}{C}-CH_3 + HCHO + R_2NH \longrightarrow$ ________.
5. 
6. Substituted dicarboxylic acids can be synthesis from ________ compound.
7. Formula Isovaleric acid is ________.
8. In the knoevengeal condersation, final compound is ________.
9. When dispessed phase is liquid and dispession medium is gas the colloidal system is called ________.
10. Brownian movement is was discovered by________.
11. Peptization denotes ________.
12. Greater the valency the higher the coagalating power of ion. This rule ware introduced by ________.
13. Curd is ________ type of colloid.
14. Smoke is an example of ________.
15. ________ ion can cause coagulation of proteins.
16. Gold number is given by ________.
17. Milk is an emulsion in which ________.
18. The emulsifying agent in milk is ________.

ANSWERS

1. Molecular orbital theory
2. Specific heats of
3. Extrinsic
4. 

   $ph-\overset{\overset{O}{\|}}{C}-CH_2$

5. $H_3C - CH = CH - COOH$
6. Malonic ester
7. 

   $CH_3 - CH(CH_3) - CH_2COOH$
8. α, β unsaturated compound
9. cloud
10. robest brown
11. breaking and dispersion into colloidal state
12. Hardy-schulze
13. Gel
14. Smoke disperred in air
15. Ag^+
16. Zsigmondy
17. Milk fat is dispered in water
18. Casein

One Mark Answers

1. Give examples of trivalent impurities used to form p-type semiconductors.

Ans :

Al, Ga, In and B.

2. Write any two dicarboxylic acids.

Ans :

Succinic acid	-	$HOOC(CH_2)_2$ CHOH
Adipic acid	-	$HOOC(CH_2)_4$ COOH

3. What is an acetacetic ester?

Ans :

Acetoacetic ester is basically an ester used as an intermediate in synthesis of many organic compounds such as drugs dyes etc.

4. Define lyophilic colloids.

Ans :

Colloids formed by directly mixing substances like gum, gelatine, starch, etc with a suitable liquid are known as lyophilic colloids.

5. List the steps involved in the preparation of colloids.

Ans :

Colloids can be prepared by following methods,

1. Chemical method.
2. Peptization.
3. Electrical disintegration (or) Bredig's arc method.

6. List the various factors affecting the adsorption of a gas on solid adsorbent.

Ans :

The various factors affecting the adsorption of a gas on a solid adsorbent are,

(a) Nature of the gas

(b) Nature of adsorbent

(c) Effect of temperature

(d) Effect of pressure

(e) Adsorbent activation.

7. Define surface chemistry.

Ans :

A branch of chemistry which deals with the chemical changes that occurs at the surface (or) interfaces is known as surface chemistry. It deals with the bulk phases of pure compounds (or) solutions.

8. What is 0/W and W/O type? Give

Ans :

O/W Type

It is oil dispersed in water type of emulsion in which oil is the dispersed phase and water is the dispersion medium.

Ex : milk, vanishing cream, etc.

W/O Type

It is water dispersed in oil type of emulsion in which water is the dispersed phase and oil is the dispersion medium.

Ex : cream, butter, etc.

Practicals

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The aim of the current exercise is to identify the functional group in the given organic compound by the following qualitative tests.

I. Preliminary tests

(i)	Physical state:	Solid/liquid.
(ii)	Physical constants:	m.p for solids/b.p for liquids
(iii)	Ignition test:	Take 2 drops of the liquid or 20 mg of the solid in a nickel spatula and heat on the flame. Sooty flame-Aromatic Non-Sooty flame - Aliphatic. Charring with smell of burnt sugar - Carbohydrates.

II. Extra elements

Lassaignes test: Heat a small piece of sodium metal in a fusion tube till it melts and becomes red hot, add compound to it and heat to red hot. Drop the fusion tube into mortar containing 5-10 ml of distilled water and cover with wire guage. Grind it along with glass pieces and filter. This is called sodium fusion extract.

Test for the presence of Nitrogen, Sulphur and Halogens in the given compound by Lassaignes test using sodium fusion extract. Detailed procedure follows.

S.No.	Experiment	Observation	Inference
1.	**Test for Nitrogen** To 2 ml of the extract add a pinch of observed. solid ferrous sulphate and heat it to boiling. Add carefully 3 or 4 drops of dil. H_2SO_4.	Prussian blue colour	Nitrogen is present.
2.	**Test for Halogens**		
	To 2 ml of the extract add 4 drops of dil. Nitric acid and heat to boil for 5 minutes. Cool and add few drops of silver nitrate.	White or pale yellow ppt.	Indicates the presence of Chloride/Bromide/Iodide
	(a) To the above ppt. add dil ammonia solution and shake.	Ppt. is soluble. Ppt. is sparingly soluble. Ppt. is insoluble.	Chloride is present Bromide is present Iodide is present
	(b) To 5-6 drops of the extract add 1 ml of CCl_4 and 1 ml of acidified $KMnO_4$ solution and shake well.	CCl_4 layer changes to orange brown colour.	Bromide is confirmed

	(c) To 5-6 drops of the extract add 1 ml of CCl_4 and 1 ml of 20% sodium nitrate solution and shake well.	CCl_4 layer changes to purple colour.	Iodide is confirmed
3.	**Test for Sulphur** To 1 ml of the extract add 1 ml of freshly prepared sodium nitroprusside $(Na_2[Fe(CN)_5NO]2H_2O$	Purple or violet red colour	Sulphur is present

Test for Nitrogen :

$$Na + C + N \xrightarrow{\qquad} NaCN$$

$$6\ NaCN + FeSO_4 \xrightarrow{\qquad} Na_4[Fe(CN)_6] + 2Na_2SO_4$$

sodium ferricyanide

$$Na_4[Fe(CN)_6] + Fe^{3+} \xrightarrow{\qquad} Fe_4[Fe(CN)_6]_3$$

ferreso ferricyanide

Test for Halogens:

$$Na + Cl \xrightarrow{\qquad} NaCl$$

$$NaCl + AgNO_3 \xrightarrow{\qquad} AgCl \downarrow + NaNO_3$$

$$Na + Br \xrightarrow{\qquad} NaBr$$

$$NaBr + AgNO_3 \xrightarrow{\qquad} AgBr \downarrow + NaNO_3$$

$$Na + I \xrightarrow{\qquad} NaI$$

$$NaI + AgNO_3 \xrightarrow{\qquad} AgI \downarrow + NaNO_3$$

Test for Sulphur:

$$Na + S \xrightarrow{\qquad} Na_2S$$

$$Na_2S + Na_2[Fe(CN)_5NO] \xrightarrow{\qquad} Na_4[Fe(CN)_5NOS]$$

III. Solubility

Test the solubility of the compound separately in water, ether, 5% aq sodium bicarbonate, 5% aq sodium hydroxide solution, dil HC1 & Cone. Sulphuric acid.

S.No	H_2O	ETHER	10% $NaHCO_3$	10% NaOH	Dih HCI	Cone. H_2SO_4	CLASS
1.	–	+	+ Brisk effervescence	+	–		Strong acid (carboxylic acid)
2.	–	+	–	+	–	+	Weak acid (Phenol)
3.	–	+	–	–	+		Bases (amines)
4.	–	+	–	–	–	+	Neutral (aldehydes, ketones, amides, anilides, esters, ethers & nitrohydrocarbons)
	+	–	–	–	–		Polynuclear aromatic and halogenated hydrocarbons.
5.	+	–	+	+	+	+	Miscellaneous (Carbohydrates, urea and thiourea)

Note:

1. The solubility of the carboxylic acid can be confirmed by re precipitating the acid by neutralizing with dil. HCI.
2. The solubility of the weak acid can be confirmed by re precipitating the acid by neutralizing with Dil. HCI.
3. Sometimes amines form salts (solids) on adding dil. HCI. In such cases water can be added to dissolve the soild, confirm the solubility by neutralizing with 10% NaOH.
4. Conc.H_2SO_4 can nearly act as a solvent for a number of neutral compounds. The solubility' in Cone, sulphuric acid may be tested only when the compound is insoluble in all other solvents. If insoluble in H_2SO_4 the compound may be a polynuclear aromatic/halogenated hydrocarbon.

V. Functional group analysis

Identify the functional groups present in the compound by qualitative tests. Wherever possible two confirmative tests should be carried out. The details are given in the table.

VI. Derivatives

Once the functional group is identified it has to be confirmed by preparing one solid derivative and by determining its melting point.

VII. Reporting

Report your observation and conclusions as below:

Based on preliminary tests, extra elements, solubility, functional group analysis and derivatives the given compound is identified and confirmed as __________

Functional Group Analysis of Carboxylic Acids.

S.No	Experiment	Observation	Inference
1.	**Solubility in sodium bicarbonate solution:** To 50mg of the compound add 1 ml of 10% sodium bicarbonate solution. To the clear solution add a few drops of Conc. HC*l*.	The compound dissolves with effervescence. The compound is regenerated.	Presence of COOH group, Compound is a carboxylic acid.
2.	**Esterification:** To 50 mg of the compound add 1 ml of ethyl alcohol or methanol and add 1 ml of Cone. H2SO4 and heat the mixture in hot water bath for 5mins. Pour the contents into cold 10% sodium bicarbonate solution.	Fruity odour.	Compound is a carboxylic acid.
3.	**Ferric chloride colouration:** To 50 mg of the compound add few drops of ammonium hydroxide until alkaline to litmus. Add 1 ml of neutral Ferric chloride solution.	A brownish violet or reddish brown ppt.	Carboxylic acid confirmed,

Derivatives of Carboxylic acid:

Esterification

Reactions of carboxylic acid

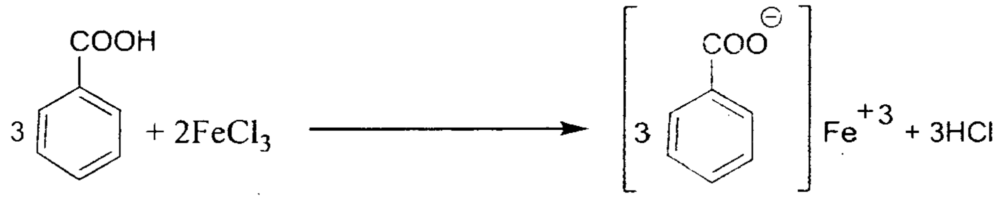
Reaction with $NaHCO_3$

$$PhCOOH + NaHCO_3 \longrightarrow PhCOONa + H_2O + CO_2\uparrow$$

Esterification

$$PhCOOH + C_2H_5OH \xrightarrow[\Delta]{Conc.H_2SO_4} PhCOOC_2H_5 + H_2O$$

Reaction with $FeCl_3$



Phenols

S.No	Experiment	Observation	Inference
1	**Neutral $FeCl_3$ test** Take 5 drops of the compound and add a few drops of freshly prepared neutral $FeCl_3$ solution.	Green/brown/violet/ blue color develops. Green color Violet color	Compound may be a phenol. (3-Naphthol Simple phenol.
2	**Phthalein fusion test:** To 100 mg of the compound in a test tube add equal amounts of Phthalic anhydride and heat. Add 2 drops of Conc. H_2SO_4. Stir the mixture, cool and add 2-3 drops of this mixture into a breaker containing 5 ml of 10% NaOH.	Pink colour develops Red/blue/fluorescent colour develops. Fluorescent green colour	Compound is phenol, Compound is a substituted phenol, (β-Naphthol
3.	**Reaction with bromine water:** To 1 drop of phenol add bromine water until orange colour persists. Pour it in a beaker containing ice cold water.	Formation of an yellowish white ppt.	Phenolic nature is confirmed.
4.	**Libermann reaction:** Take 1 or 2 crystals of $NaNO_2$ in a dry test tube, add 0.5 gms of phenol and heat for 1ml Allow it to cool and add twice the volume of Conc. H_2SO_4.	Deep green or deep blue colour develops which on dilution changes to red colour.	Phenolic nature is confirmed,

5.	**Diazotisation:** Take 2 or 3 drops of aniline in a test tube, add Conc. HCl until aniline dissolves and add 3 ml of cold water cool the test tube in ice to 0°C. Add few drops of 20% $NaNO_2$ solution (which is also cooled to 0°C) to the aniline solution. Add this diazonium solution to a cold solution of phenol in 10 ml of 10% NaOH solution. Maintain the temperature at 0°C.	Formation of a red orange dye.	Confirms phenol.

Derivatives:

A. Bromo derivative

Transfer 1 gm of the phenol into a beaker and dissolve in 3 ml of methanol if the compound is a solid, then add Br_2 in acetic acid until red colour of Br_2 is persistent. Keep aside for 5-10 mins. Add ice cold water to the mixture and filter the solid separated out.

Note: Do not prepare bromo derivative for β-Naphthol. Instead Neroline can be prepared as derivative for it

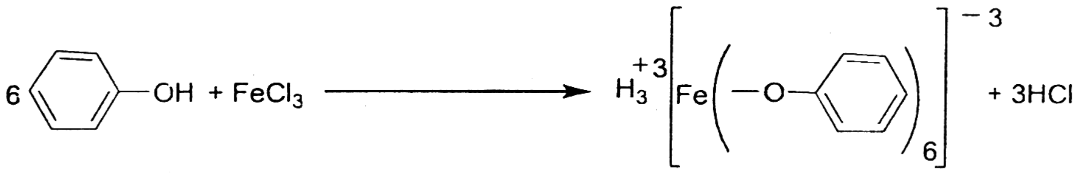
B. Benzoyl derivative

Transfer 500 mg of the compound in to a conical flask and add 10 ml of 15% NaOH solution and shake the mixture till all the phenol dissolves in the NaOH, then add 2ml of Benzoyl chloride and cork the flask, shake the flask vigorously for 10 mins, where by solid benzoyl derivative separates out. Filter and wash with 10% sodium carbonate solution to remove excess of Benzoyl chloride and again wash with water to remove the carbonate.

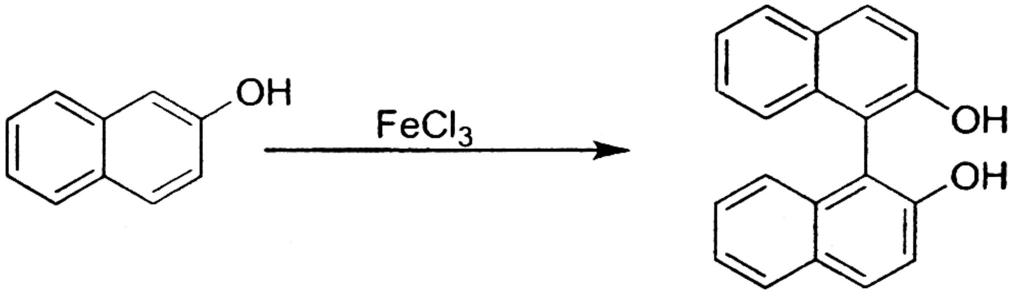
Note: 2-chlorophenols do not give benzoyl derivative.

Reactions of Phenol

Reaction with $FeCl_3$

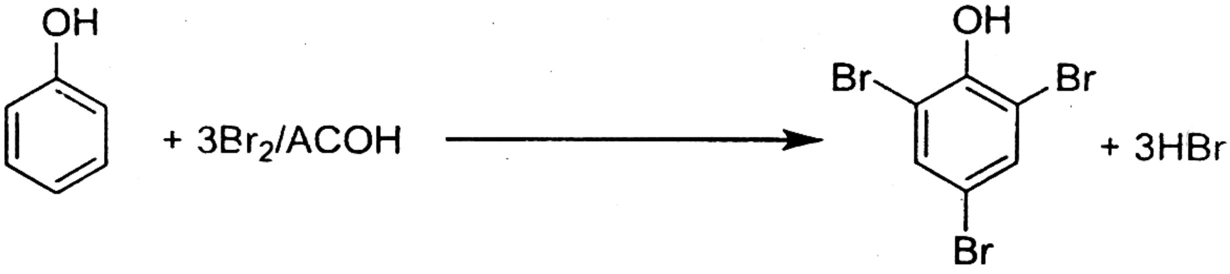


Violet (Complex ion)

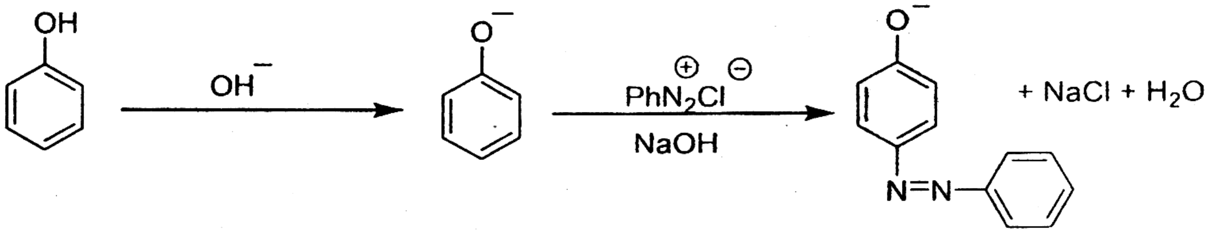


α- di-naphthol
(Green)

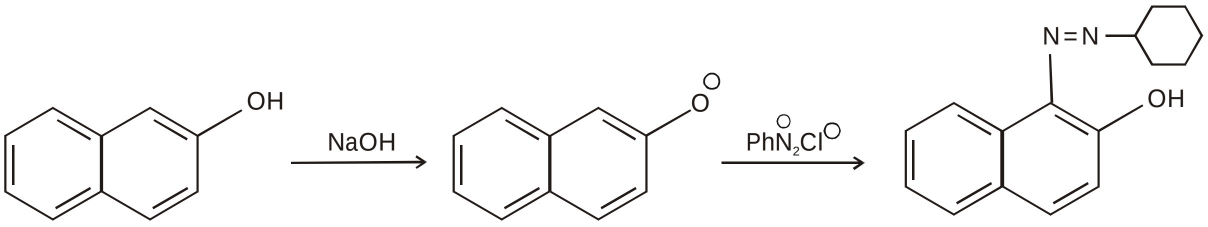
Bromination



Diazotization

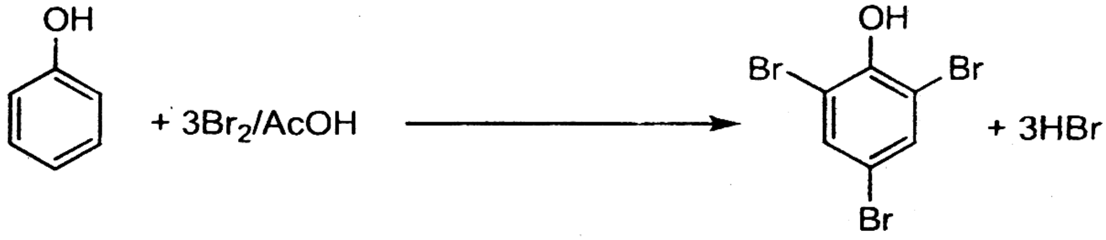


Orange red Azo dye

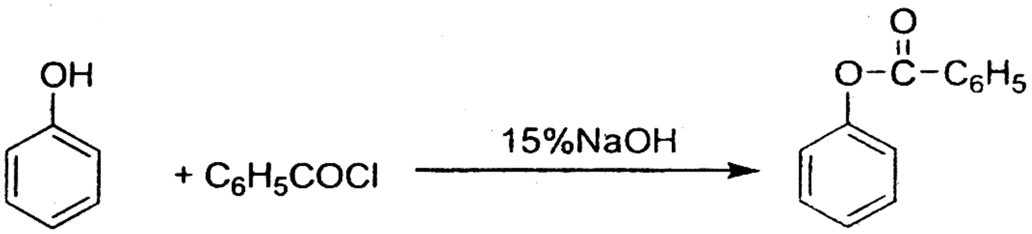


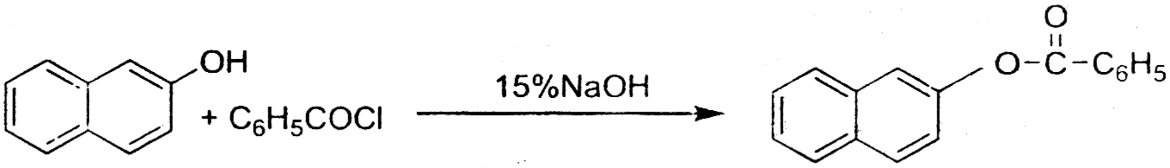
Orange Azo dye

Bromination

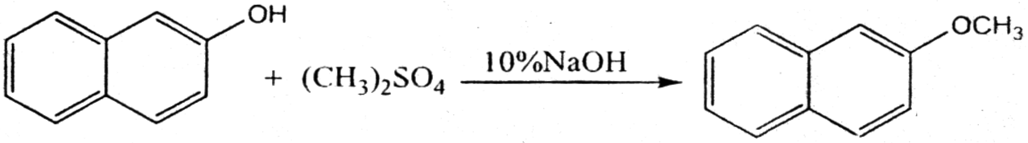


Benzoylation





Methylation



Amines :

S.No	Experiment	Observation	Inference
1.	**Solubility in dil. HC1** Take 10 mg(5 drops) of the compound and add 5 ml of dil.HCl.	The compound dissolves and a clear solution is obtained.	The compound may be primary/secondary/ tertiary amine.
2.	**Isocyanide reaction** Add 0.5 ml of chloroform to about 0.5 ml of the given compound and add 2-3 ml compound and add 2-3 ml of alc.KOH or NaOH. Mix well and warm on waterbath.	A foul smell of isocyanide (carbylamine) is observed. The foul smell is destroyed by adding Conc, HC1.	Primary amine is confirmed,

3.	**Nitrous acid test:** Dissolve 50 mg of the substance in 1 ml of substance in 1 ml of Conc. HC1 and dilute HC1 and dilute with 3 ml of water. Cool in ice and add few drops of cold $NaNO_2$ solution.	If liberation of brown gas with the formation of an orangish brown solution.	Indicates the formation of diazonium ion. Primary amine is confirmed.
4.	**Reaction with bromine water:** To 1 drop/10 mg of amine add bromine in acetic acid until orange colour persists. Pour it in a beaker containing ice cold water.	Formation of white ppt.	Primary amine is confirmed,
5.	**Diazotisation of primary amine:** Test as for phenols	Azo dye is formed.	Primary amine is confirmed.

Derivatives:

1. **Primary amine:**

Bromo derivative: Transfer 1 ml of the primary amine into a beaker and add Br_2 in acetic acid until red colour of Br_2 is persistent. Keep aside for 5-10 mins. Add ice cold water to the mixture where by a white/yellow ppt. separates out.

Reactions of Amines:

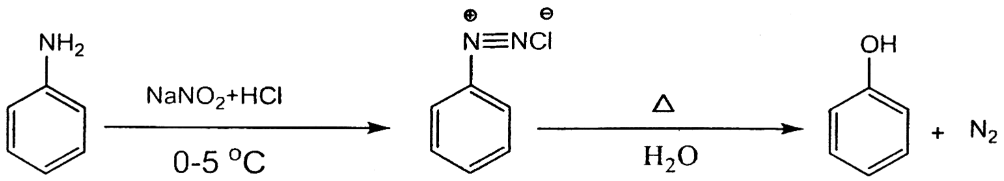
Reaction with HC***l*** **:**

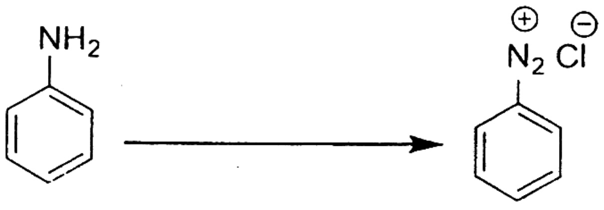
$$Ph\text{-}NH_2 + HCl \longrightarrow ph\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$$

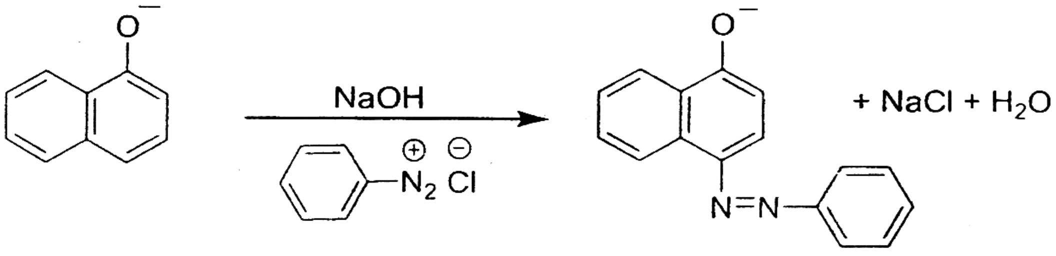
Isocyanide test :

$$PhNH_2 + CHCl_3 + 3KOH \longrightarrow PhNC + 3KCl + 3H_2O$$

Diazotization :

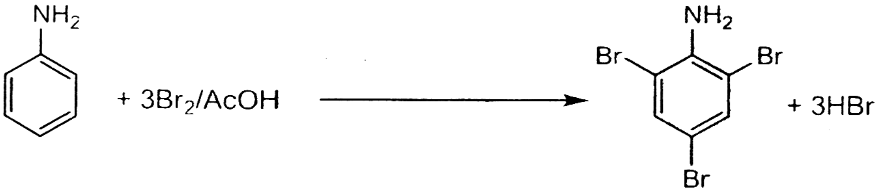






Orange red Azo dye

Bromination



Carbonyl Compounds :

S.No	Experiment	Observation	Inference
1.	**2,4-DNP test:** dissolve 2-3 drops of compound in alcohol, add 1 ml of 2,4 DNP reagent (if compound is solid dissolve it in few drops of methanol). Keep it in hot water bath for few mins.	An orange ppt. of 2.4-Dinitro phenyl hydrazine is formed.	Carbonyl compound is present.
2.	**Tollens test:** To 1 ml of compound add 5 ml of Tollens reagent and heat on water bath.	A silver mirror is deposited (or black ppt.)	Aldehyde group is confirmed.
3.	**Fehlings test:** To 1 ml of compound add I ml of Na_2CO_3 solution and 1 ml of Fehlings solution A and 1 ml of Fehlings solution B. Boil the mixture on water bath.	Red coloured ppt. is formed immediately. Red ppt is formed after heating for 20 minutes.	Confirms aliphatic aldehyde. Confirms aromatic aldehyde.
4.	**Bisulphite addition reaction:** To I ml of compound dissolved in alcohol add 1 ml of saturated sodium bisulphite solution, heat on water bath. Then cool in ice.	White addition product is formed.	Aldehyde or ketone,

Note:

If all the tests are negative except 2,4-DNP test then the compound may be ketone.

Preparation of Tollens reagent:

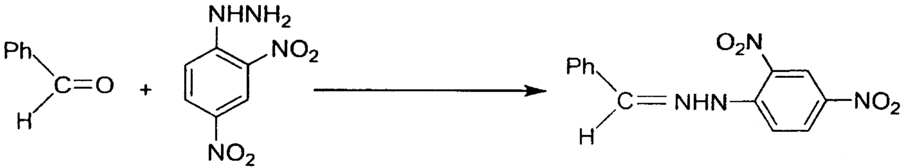
Take 5ml of $AgNO_3$ solution in a clean test tube and add 2 drops of 10% NaOH solution. A grey ppt. is formed. To this add NH_4OH drop wise until the grey ppt. just dissolves. This is known as Tollens reagent.

Iodoform test for methyl ketone:

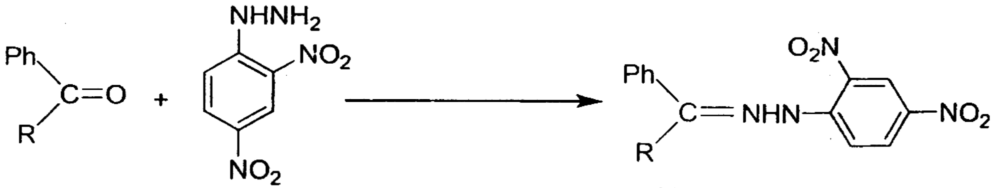
S.No	Experiment	Observation	Inference
1.	To 2-3 drops of compound add 1 ml of water, add 1,4-dioxane till clear solution is obtained. Then add I ml NaOH followed by I_2 in KI till the colour of Iodine persists. Heat on electric hot water bath. Then, cool in ice. Scratch the inner walls of the test tube with a glass rod.	Yellow ppt is formed	Methyl ketone is confirmed,

Reactions of Carbonyl compounds:

2,4 DNP test



Yellow Orange soild



Yellow Orange soild

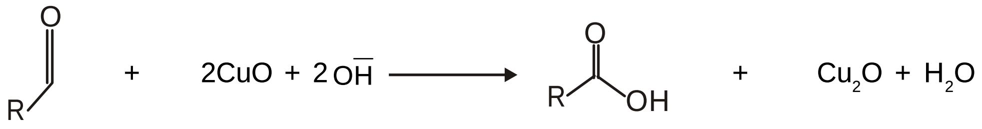
R = CH_3, Ph

Tollen's test

$$2AgNO_3 + 2NaOH \longrightarrow Ag_2O + 2NaNO_3 + H_2O$$

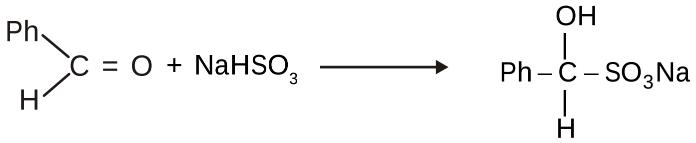
$$Ag_2O + 4NH_4OH \longrightarrow 2\left[Ag(NH_3)_2\right]^+ \overline{OH} + 3H_2$$

Fehling's test

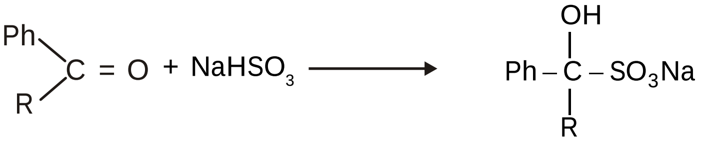


Aldehyde Fehling's solution Carboxylic acid Red precipitate

Bissulphite addition test



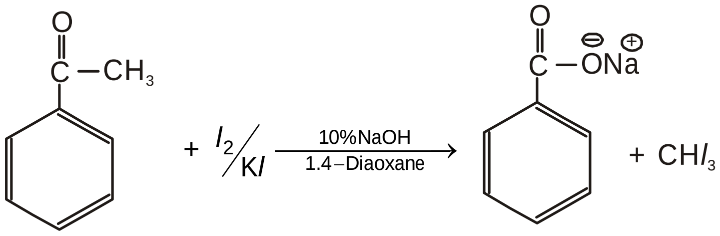
White crystaline solid



White crystaline solid

R = CH_3, Ph

Iodoform test



Amines

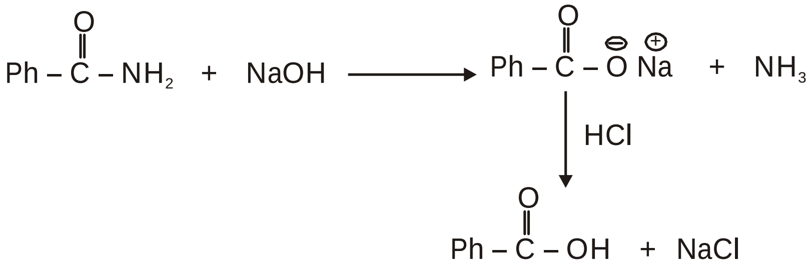
S.No	Experiment	Observation	Inference
1.	**Hydrolysis:** Take 5mg of compound in a test tube and add 2 ml of NaOH and heat for 2 mins on a burner (test with litmus) Add Conc. HCl to the above alkaline solution.	Ammonia gas is liberated. Turns red litmus to blue White ppt. of carboxylic acid forms.	Amide is confirmed

Derivatives:

Hydrolysis of amide:

Transfer 1 grn of amide in to a conical flask, add 15 ml of 20% NaOH solution and heat it on a Bunsen burner till the mixture boils. Cool the reaction mixture and neutralize with Cone. HC*l*. A white ppt. of carboxylic acid separates out with loss of ammonia.

Reactions of Amide:



$$Ph-\overset{O}{\overset{\|}{C}}-NH_2 + NaOH \longrightarrow Ph-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\,\overset{\oplus}{Na} + NH_3$$

$$\xrightarrow{HCl} Ph-\overset{O}{\overset{\|}{C}}-OH + NaCl$$

Nitro Hydrocarbons:

S.No	Experiment	Observation	Inference
1.	**Barker-Mullikon test:** Dissolve 50mg of the compound in 1 ml of ethanol and add 50 mg of solid NH_4Cl and 50mg of zinc dust. Heat the mixture to boiling, filter. To the filtrate add Tollens reagent and heat it on the water bath.	Black or grey ppt. / silver mirror formation.	Nitro hydrocarbon confirmed.

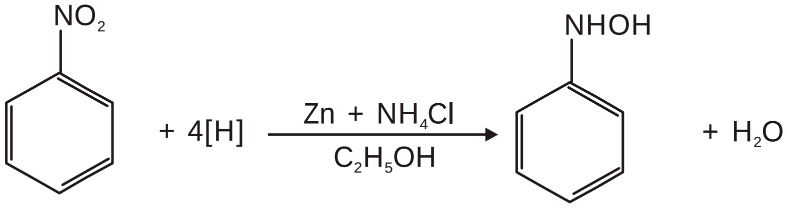
Derivative:

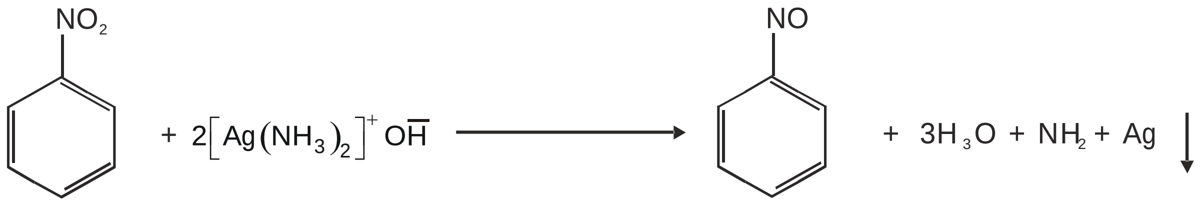
Dinitration:

Transfer 1 ml of nitrobenzene into a small round bottomed flask, then add nitrating mixture (2 ml of fuming HNO_3 + 3ml of Cone. H_2SO_4) to it and heat the mixture on water bath with an air condenser for 40 min. Transfer the reaction mixture into a beaker containing cold water. Pale yellow solid of m-dinitrobenzene separates out.

Reactions of Nitro hydrocarbons:

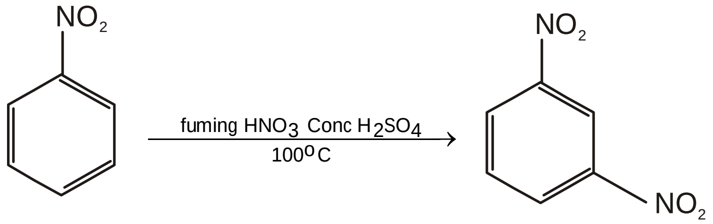
Barker Mullikhan Test:





Derivative

Nitration :



Esters

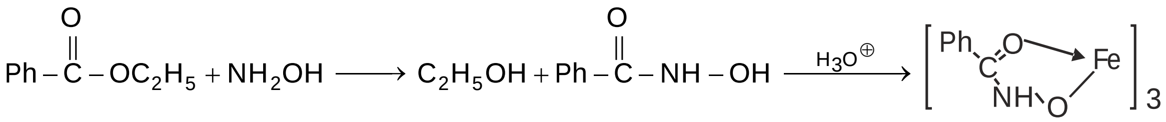
S.No	Experiment	Observation	Inference
1.	**Hydroxamic acid test:** To a drop of the compound add 100 mg of solid hydroxyl amine hydrochloride and 5 ml of 10% NaOH solution. Boil the mixture on a Bunsen flame for 2-3 min. Cool and acidify with dil. HC1. To this solution add few drops of neutral $FeCl_3$ solution.	Deep violet or deep reddish colour develops due to the formation of hydroxamic acid.	Ester is confirmed.
2.	**Hydrolysis:** Take 2ml of ester in a 50 ml round bottomed flask and add 20ml of 30% NaOH solution and reflux using a water condenser for half an hour. Cool the mixture and neutralize with Conc. HC1.	Ester undergoes hydrolysis to give an alcohol and acid. The alcohol being liquid floats on the mixture and acid gets ppt. by neutralisation.	Ester is confirmed.

Derivatives:

Hydrolysis: Take 2 ml of ester in a 50ml round bottomed flask and add 20 ml of 30% NaOH solution and reflux using a water condenser on a Bunsen burner for one hour. If there are no oily drops floating on the surface then it indicates the reaction is complete. Otherwise continue the heating for some more time. Then transfer the reaction mixture into a 250ml beaker and neutralize with Conc. HC*l* while cooling. A white ppt. of aromatic carboxylic acid separates out.

Reactions of Esters:

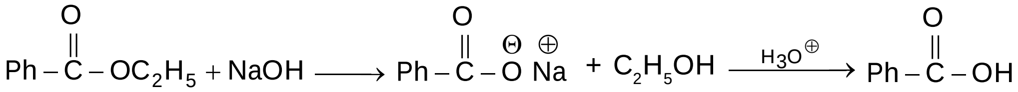
Hydroxamic Acid Test:



$$Ph-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NH_2OH \longrightarrow C_2H_5OH + Ph-\overset{O}{\overset{\|}{C}}-NH-OH \xrightarrow{H_3O^{\oplus}}$$

Magenta Complex

Hydrolysis:



$$Ph-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NaOH \longrightarrow Ph-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}\ \overset{\oplus}{Na} + C_2H_5OH \xrightarrow{H_3O^{\oplus}} Ph-\overset{O}{\overset{\|}{C}}-OH$$

Polynuclear Aromatic Hydrocarbon:

S.No	Experiment	Observation	Inference
1.	**Test with $AlCl_3$** To a few mg of the compound or 0.2 ml of liquid add 3ml $CHCl_3$ and of test tube, shake well. Then transfer a pinch of $AlCl_3$ into a dry test tube and sublime.	Orange colour develops on the sides of the test	Compound may be halo hydrocarbon.
	Then add $CHCl_3$ to the sublimed $AlCl_3$ such that the $CHCl_3$ layer touches the $AlCl_3$	Purple or blue or green colour develops.	Compound may be poly hydrocarbon.

Derivatives:

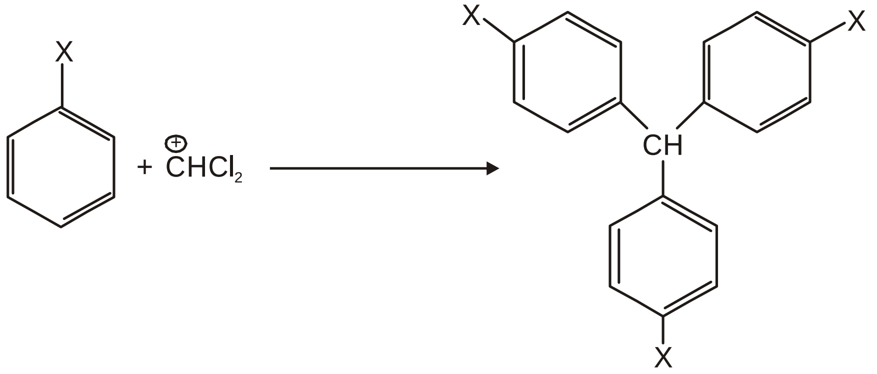
Nitration: To 1 ml of hydrocarbon add a mixture of 2ml of Conc.HNO_3 and 4ml of Cone. H_2SO_4 and heat the mixture on water bath for 20 min. and transfer the mixture into a beaker containing cold water.

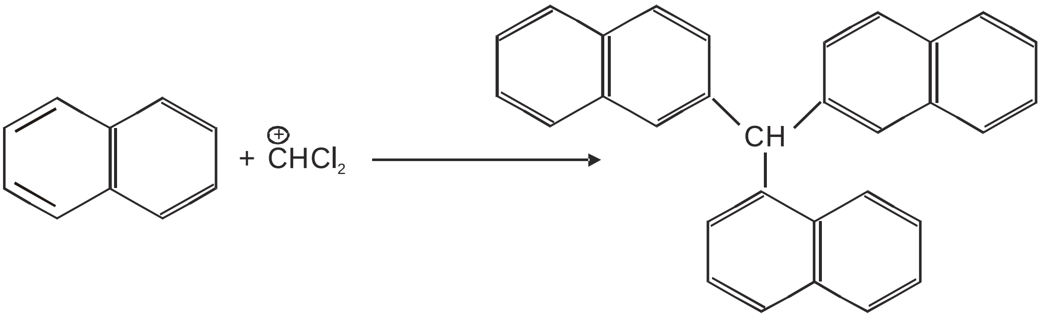
Reactions of Hydrocarbons:

Test with $AlCl_3$:

$$CHCl_3 + AlCl_3 \longrightarrow \overset{\ominus}{AlCl_4} + \overset{\oplus}{CHCl_2}$$

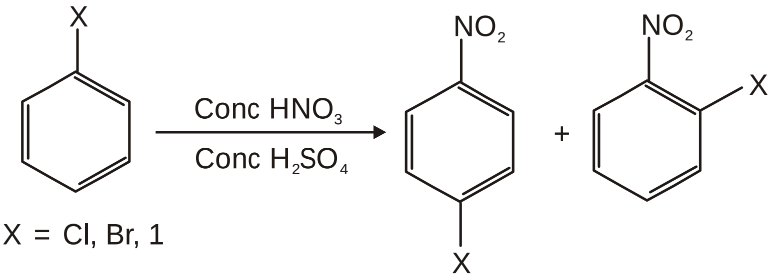
$$3C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} (C_6H_5)_3\overset{\oplus}{C}\ \overset{\ominus}{AlCl_4} + 3\ HCl$$

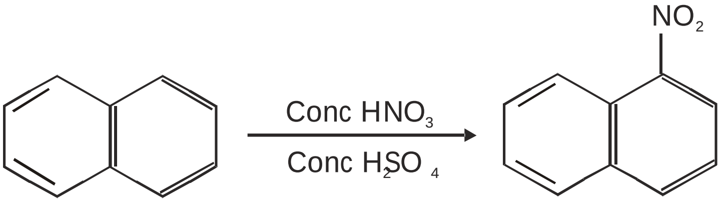




Derivative :

Nitration :





Miscellaneous Group

A : CARBOHYDRATES:

S.NO.	Experiment	Observation	Inference
1.	**2,4-DNP test :** Dissolve 5 mg of the compound 1 ml of water, add 1 ml of 2,4-DNP reagent. If orange ppt. does not devlope immediately, heat on water bath and cool in ice	Orange ppt.	Presence of carbonyl group.
2.	**Molish test :** Dissolve 2mg of the compound in 4 ml of water and add 3-4 drops of alc. α-Naphthol. Then add 2ml of conc. H_2SO_4 carefully from the sides of the test tube. Do not shake the test tube.	A deep violet colour is formed at the junction of two layers.	Carbohydrate is confirmed.
3.	**Tollens test :** Dissolve 1 mg of the compound in 1ml of water and add 1 ml of Tollens reagent. Heat the mixture on water bath for 5-10 min.	Silver mirror is deposited No silver mirror.	Aldose is confirmed ketose is confirmed
4.	**Rapid furfural test :** Dissolve 20 mg of the compound in 1 ml of water and add 1 ml of α -Naphthol solution and 2-3 drops of Conc. HCl. Heat on hot water bath.	In case of fructose violet colour is formed immediately. If the colour is developed slowly at RT but develops on heating in a water bath	May be fructose. May be glucose

Derivatives :

Carbohydrates :

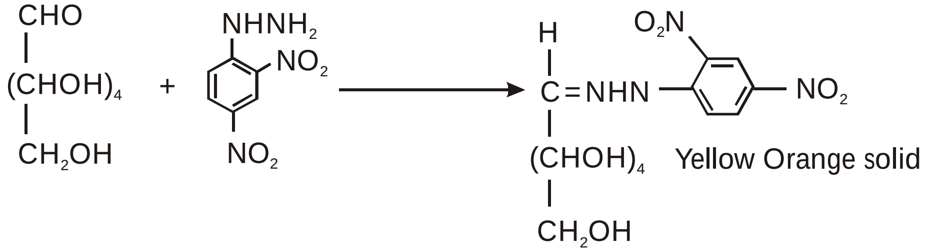
Osazone derivative :

Prepare saturated solution of carbohydrate in 5 ml of water, thenadd 3 ml of glacial acetic acid and 5 ml of phenyl hydrazine in a boiling tube and heat on water bath for 15 min. An yellow crystalline phenyl osazone separates out.

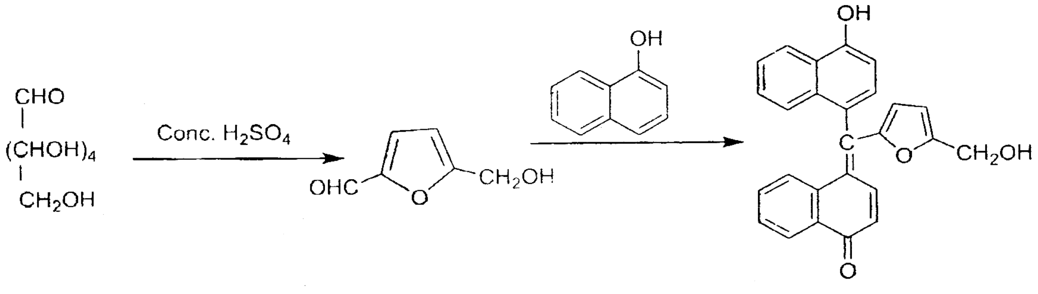
Note : Dissolve phenyl hydrazine hydrochloride in sodium acetate, solution. Then add to carbohydrate solution.

Reaction of Carbohydrate

2,4 - DNP test :

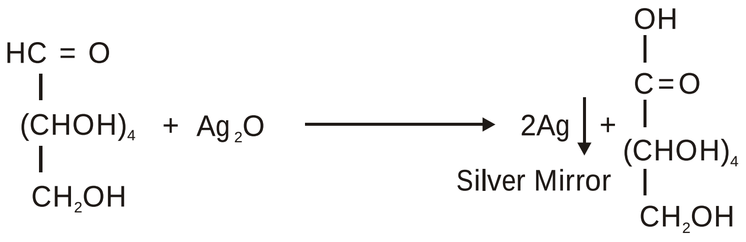


Molish Test :



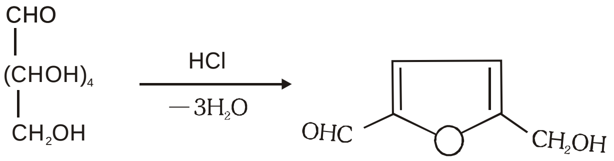
Violet colour

Tollens test :

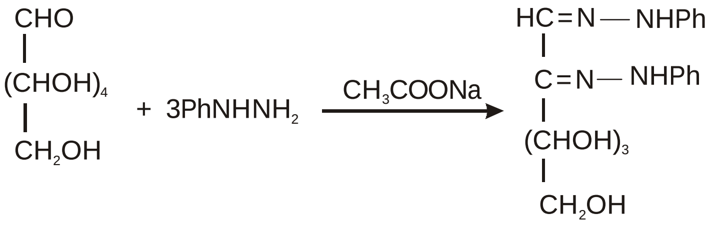


$$\begin{array}{l} HC=O \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + Ag_2O \longrightarrow \underset{\text{Silver Mirror}}{2Ag\downarrow} + \begin{array}{l} OH \\ | \\ C=O \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Rapid Furfural Test :



Osazone :



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + 3PhNHNH_2 \xrightarrow{CH_3COONa} \begin{array}{l} HC=N—NHPh \\ | \\ C=N—NHPh \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

Osozone (Yellow)

B. Urea

S.No.	Experiment	Observation	Inference
1.	**Biuret test :** Heat 0.1 gm of the compound in a dry test tube till the substance sublime evolving vapours with strong pungent odour. To the colourless solid add 2ml of distilled water, 1-2 drops of very dilute copper sulphate solution, strin and mix it with 2 ml of dilute NaOH solution.	Vapour has characteristic smell of ammonia and a colourless solid of biuret is formed. A violet red colour solution is observed	Urea is confirmed.

Derivatives for Urea :

a. Urea nitrate:

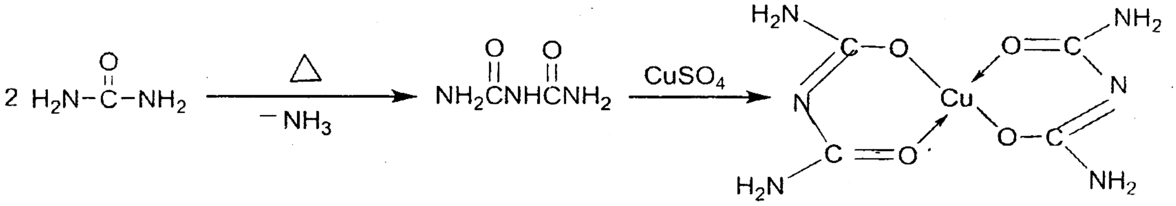
To 0.1 mg of the compound dissolved in 3-4 ml of water taken in a test tube, add 3-4 drops of Conc. Nitric acid and scratch the sides with a glass rod. Warm if necessary in a hot water bath, on cooling a colourless bulky solid urea nitrate separates out, filter at the pump, wash a little cold water and allow it to dry.

b. Urea oxalate

Dissolve 1 gm of urea in 3-4 ml of water and mix it with a few drops of saturated oxalic acid solution. Warm if necessary, cool and scratch the test tube with a glass rod. A crystalline solid separates out. Filter the product, wash with cold water and allow it to dry.

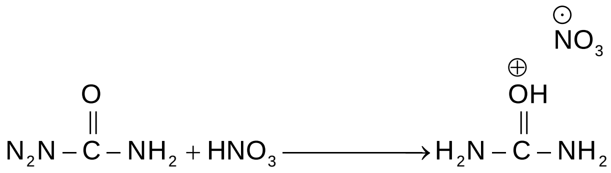
Reactions of Urea

Biuret Test :



Purple coloured compex

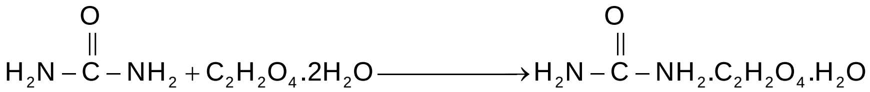
Nitration :



$$N_2N-\overset{\overset{\Large O}{\|}}{C}-NH_2 + HNO_3 \longrightarrow H_2N-\overset{\overset{\overset{\odot}{NO_3}}{\overset{\oplus}{OH}}}{\|}}{C}-NH_2$$

UreaNitrate

Urea Oxalate :



$$H_2N-\overset{\overset{\large O}{||}}{C}-NH_2+C_2H_2O_4.2H_2O \longrightarrow H_2N-\overset{\overset{\large O}{||}}{C}-NH_2.C_2H_2O_4.H_2O$$

VII. Reporting :

Based on preliminary tests, extra elements,solubility, functional group analysis and derivatives the given compound is identified and confirmed as _________.

1. Physical state of the mixture

   i. Solid-Solid

   ii. Solid-Liquid

   iii. Liquid-Liquid

2. **Solubility**

One of the component in a binary mixture may be soluble in any one of the reagent- $NaHCO_3$/ NaOH/ Dil. HC1. Based on its solubility the mixture is separated into individual components. If one of the component is insoluble in ether then ether will be the separating reagent.

S.No.	Ether	10% $NaHCO_3$	10% NaOH	Dil. HCl	Separating reagent
1	+	+	+	–	$NaHCO_3$
2	+	–	+	–	NaOH
3	+	–	–	+	HC1
4	–				Ether

Solubility Procedures

Take about 100 mg of the given mixture in a test tube and then add 10 % $NaHCO_3$ solution. Shake well and filter. To the Liberate add Conc. HCl for neutralization. Upon neutralization if one of the component separates that indicates that the separating reagent for the mixture is 10 % $NaHCO_3$ and if nothing separates on neutralization that indicates the mixture is insoluble in 10% $NaHCO_3$. Then repeat the procedure with 10% NaOH. If NaOH is also negative then repeat the same procedure with Dil. HC1 and neutralize with NaOH.

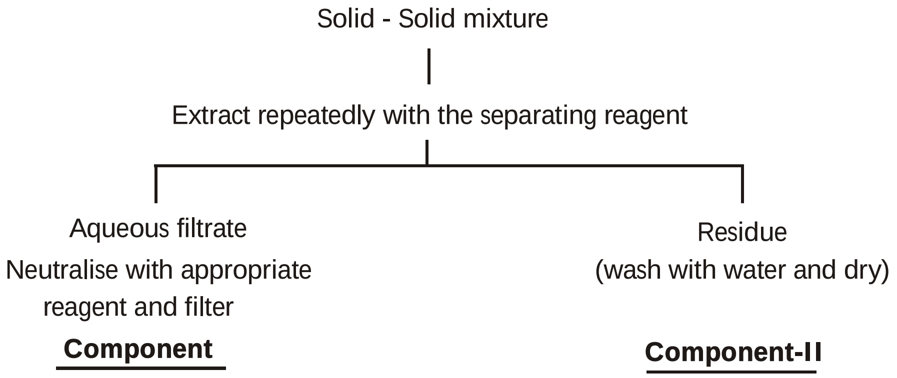
Separating procedure

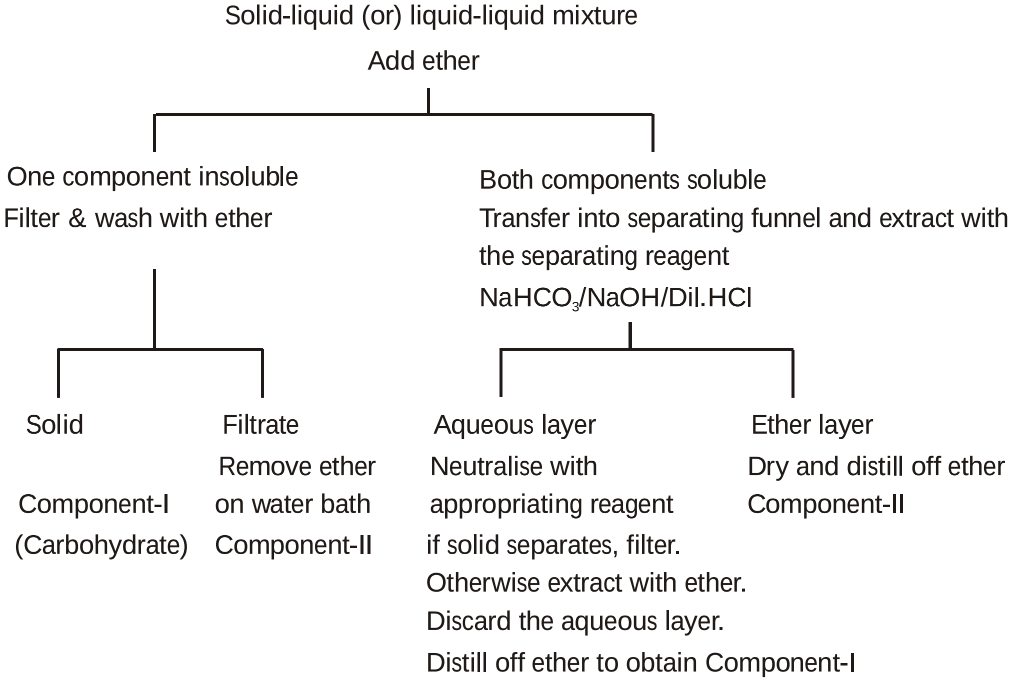
1. **Solid-solid mixture**

Transfer the entire mixture into a conical flask and repeatedly extract with the reagent in which the mixture is soluble ($NaHCO_3$/NaOH/ Dil. HC1) and filter, The completion of the mixture separation is checked by neutralization of the last drops of the filtrate. If no solid separates that indicate the completion of separation and if solid separates the process is to be repeated until no precipitation occurs on neutralization. After the separation combine all the filterates, neutralize and filter. The solid obtained is component-I. The solid insoluble in the reagent is component-II which is washed thoroughly with water and dried.

2. **Solid-liquid mixture/ Liquid-liquid mixture**

Transfer the mixture into a beaker, add ether and stir well. If one of the component is insoluble in ether then ether is the reagent for separation. If both the components are soluble in ether, transfer the mixture into a separating funnel and check the solubility in $NaHCO_3$/NaOH Dil. HC1. Separate the mixture based on its solubility.





The possible combinations of binary mixtures are

(i) Strong acid + Neutral including Hydrocarbons

(ii) Strong acid + Weak acid

(iii) Weak acid + Neutral including Hydrocarbons

(iv) Base + Hydrocarbon

(v) Carbohydrate + Weak acid

(vi) Carbohydrate + Strong acid

FACULTIES OF SCIENCE

B.Sc. II Year IV Semester (CBCS) Examination

Model Paper - I

CHEMISTRY - IV

Time : 3 Hours] [Max. Marks : 80

PART- A (8 × 4 = 32 M)

[Short Answer Type]

Note : Answer any Eight of the following questions

ANSWERS

1. What are Low Spin - High Spin Complexes? **(Unit-I, SQA-1)**
2. Draw the structure of Hemoglobin. **(Unit-I, SQA-9)**
3. Write the biological significance of Na, Mg and Ca. **(Unit-I, SQA-10)**
4. Write the confirmation structures for Glucose and Fructos. **(Unit-II, SQA-5)**
5. Write the Neutral Amino Acids with examples. **(Unit-II, SQA-9)**
6. Write the Heterocyclic Amino Acids with examples. **(Unit-II, SQA-12)**
7. What is Half-life Period of a First Order Reaction ($t_{1/2}$) **(Unit-III,SQA-3)**
8. What are pseudo molecular reactions? Give one example. **(Unit-III, SQA-4)**
9. What is the term quantum yield ? **(Unit-III, SQA-7)**
10. Write about n-type and p-type semiconductors. **(Unit-IV, SQA-3)**
11. Write the mannich reaction. **(Unit-IV, SQA-4)**
12. State and explain Hardy–Schulze law. **(Unit-IV, SQA-10)**

SECTION - B (4 × 12 = 48 M)

[Essay Answer Type]

Note : Answer all the following questions

13. (a) Explain the splitting pattern of d-orbitals in octahedral. **(Unit-I, Q.No.2)**

OR

(b) Explain the determitation of composition it a complex by mole ratio method. **(Unit-I, Q.No.16)**

14. (a) Give the evidences for straight chain of pentahydroxy aldehyde structure of Glucose. **(Unit-II, Q.No.2)**

OR

(b) Explain the aromaticity and resonance structures of the following. **(Unit-II,Q.No.32)**

15. (a) Derive an expression for the rate constant of a first order reaction.
Give two examples for first order reaction. **(Unit-III, Q.No.6)**

OR

(b) Discuss the terms in Jablanski diagram. **(Unit-III, Q.No.21)**

16. (a) Discuss the Free electron theory. **(Unit-IV, Q.No.2)**

OR

(b) Write about protective colloids, gold number and Hardy–Schulze law. **(Unit-IV, Q.No.18)**

FACULTIES OF SCIENCE

B.Sc. II Year IV Semester (CBCS) Examination

Model Paper - II

CHEMISTRY - IV

Time : 3 Hours] [Max. Marks : 80

PART- A (8 × 4 = 32 M)

[Short Answer Type]

Note : Answer any **Eight** of the following questions

ANSWERS

1. What are Low Spin - High Spin Complexes? **(Unit-I, SQA.1)**
2. Write the detection of complex formation by Conductivity Measurement (Marked Drop in Conductivity) **(Unit-I, SQA-6)**
3. Write the biological significance of Na, Mg and Ca. **(Unit-I,SQA-10)**
4. Write the Haworth Cyclic structures for glucose. **(Unit-II, SQA-6)**
5. Write the Neutral Amino Acids with examples. **(Unit-II, SQA-9)**
6. Write about chi-chibabin reaction. **(Unit-II, SQA-20)**
7. Define rate of a reaction and order of reaction. **(Unit-III, SQA-1)**
8. What are pseudo molecular reactions? Give one example. **(Unit-III, SQA-4)**
9. Write the differences between thermal and photochemical reactions. **(Unit-III, SQA-8)**
10. Write the Limitations of VBT theory. **(Unit-IV, SQA-1)**
11. Write the Michel addition reaction. **(Unit-IV,SQA-5)**
12. What ate Lyophilic Colloids and Lyophobic Colloids? **(Unit-IV, SQA-7)**

SECTION - B (4 × 12 = 48 M)

[Essay Answer Type]

Note : Answer all the following questions

13. (a) Write the splitting pattern of d-orbitals in square planer complex. **(Unit-I, Q.No.3)**

OR

(b) Explain the applications of HSAB. **(Unit-I,Q.No.13)**

14. (a) Describe the proof for the ring size in glucose. **(Unit-II, Q.No.7)**

OR

(b) Write any three electrophilic substitution reactions of pyrrole, furan and thiophene. **(Unit-II, Q.No.34)**

15. (a) Explain the factors effecting on the rate of reactions. **(Unit-III,Q.No.5)**

OR

(b) Derive an expression for the second order reaction and write the characteristics. **(Unit-III,Q.No.9)**

16. (a) Discuss in detail the Bond theory of metals. **(Unit-IV, Q.No.3)**

OR

(b) Mention the synthetic applications of aceto acetic ester. **(Unit-IV, Q.No.9)**

FACULTIES OF SCIENCE

B.Sc. II Year IV Semester (CBCS) Examination

Model Paper - III

CHEMISTRY - IV

Time : 3 Hours] [Max. Marks : 80

PART- A (8 × 4 = 32 M)

[Short Answer Type]

Note : Answer any Eight of the following questions

		ANSWERS
1.	What is Crystal Field Stabilization Energy?	**(Unit-I, SQA-2)**
2.	What are the para, dia and ferromagnetic substances?	**(Unit-I, SQA-4)**
3.	What are Essential Elements?	**(Unit-I, SQA-8)**
4.	Write the Tollen's Test and Fehling's Test reactions in glucose.	**(Unit-II, SQA-2)**
5.	What is zwitter ion?	**(Unit-II, SQA-14)**
6.	Write the Resonancre structures of Thiophene	**(Unit-II, SQA-19)**
7.	Give the examples of Zero order reactions.	**(Unit-III, SQA-6)**
8.	Write the effect of temperature in a rate of reaction.	**(Unit-III, SQA-2)**
9.	What is photosensitization? Give one example.	**(Unit-III, SQA-9)**
10.	Give the Limitations of free electron theory.	**(Unit-IV, SQA-2)**
11.	Write the Synthetic applications of Malonic ester.	**(Unit-IV, SQA-6)**
12.	What is gold number ?	**(Unit-IV, SQA-9)**

SECTION - B (4 × 12 = 48 M)

[Essay Answer Type]

Note : Answer all the following questions

13. (a) Explain d-orbital splitting in Tetrahedral complexes. **(Unit-I,Q.No.4)**

OR

(b) Explain the structure of Hemoglobin and the importance of Haemoglobin. **(Unit-I, Q.No.24)**

14. (a) Write the Haworth Cyclic structures for glucose & fructose. **(Unit-II, Q.No. 13)**

OR

(b) Write the classification of aminoacids with examples. **(Unit-II, Q.No.20)**

15. (a) Write the derivation for the zero order reaction and give the characteristics. **(Unit-III, Q.No.10)**

OR

(b) Discuss the photochemistry of $H_2 - Cl_2$ and $H_2 - Br_2$ reactions? **(Unit-III, Q.No.22)**

16. (a) Write a short notes on Semiconductors. **(Unit-IV, Q.No.4)**

OR

(b) Explain the electrical property of colloids. **(Unit-IV, Q.No.19)**