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CHEMISTRY STUDY CAPSULE FOR CLASS – XII
SESSION – 2022-23

CHAPTERS INCLUDED –

1. **SOLUTIONS – 7 MARKS**
2. **CHEMICAL KINETICS – 7 MARKS**
3. **d- & f- BLOCK ELEMENTS – 7 MARKS**
4. **COORDINATION COMPOUNDS – 7 MARKS**
5. **AMINES – 6 MARKS**
6. **BIOMOLECULES – 7 MARKS**

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SOLUTIONS

TWO MARKS QUESTIONS

1. Define the term molarity and molality. What is the effect of temperature on these concentration terms?
   Ans – No of moles of solute in 1 litre of solution is molarity whereas no of moles of solute in 1 kg of solvent is called molality. Molality does not change with temperature whereas molarity changes because M depends on volume and volume changes with temperature change.
2. State Henry's law and explain the effect of it solubility of gases in liquids.
   Ans – "Solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution". More the value of K_H, less will be the solubility of the gas.
3. State Roult's law if (i) both the components of a solution is volatile and (ii) solution contains a non-volatile solute.
   Ans – (i) Partial vapour pressure of each component in the solution is directly proportional to its mole fraction present in the solution.
   (ii) The vapour pressure of the solution containing non-volatile solute is directly proportional to the mole fraction of solvent only.
4. Compare ideal and non-ideal solutions.
   Ans -

Ideal solutions	Non-ideal solution
Obeys Roult's law.	Does not obey Roult's law.
ΔVmix & ΔHmix both = 0	ΔVmix & ΔHmix both $\neq$ 0
n- hexane & n- heptane, bromoethane & chloroethane	Ethanol & water, acetone & chloroform

5. Compare non-ideal solutions showing positive and negative deviations.
   Ans -

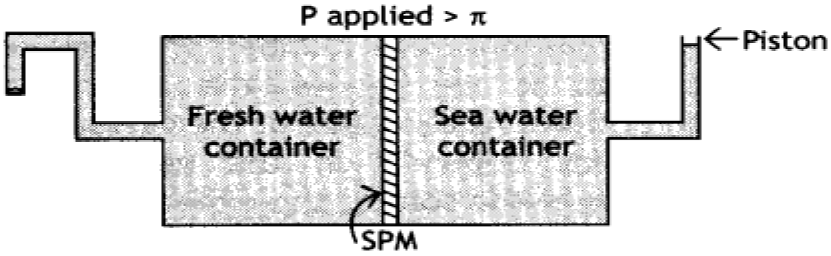
Positive deviation	Negative deviation
Observed V.P. > calculated V.P.	

A-B interaction decreases.	A-B interaction increases.
Minimum boiling azeotrope is formed.	Maximum boiling azeotrope is formed.
Water & Ethanol.	Chloform & Acetone.

6. What is abnormal molar mass? How will it be corrected?
   Ans – Due to association or dissociation of solute particles in the solution the molar mass observed is found different from actual molar mass of the solute. Now the observed molar mass is called abnormal molar mass. It will be corrected using vant-Hoff's factor while using calculation of molar mass of solute using any colligative property.
7. What will be vant-Hoff factor for the followings?
   (a) Acetic acid in water (b) Acetic acid in benzene (c) K4[Fe(CN)6] in water.
   Ans – (a) More than 1 (b) less than 1 (if 100% dimerization takes place). (c) 5 if 100% ionisation.
8. To find the molar mass of biomolecules, osmotic pressure method is preferred. Justify.
   Ans – because using osmotic pressure method temperature of the solution does not change and therefore correct molar mass is calculated whereas other methods are based on temperature change and therefore the biomolecules may decomposed or denaturized.
9. Arrange the following solutions in increasing order of boiling points and freezing points. Give justification also.
   0.1 M KCl AND 0.1 M glucose.
   Ans – B.P. = 0.1 M glucose < 0.1 M KCl – because KCl is ionized in solution and gives approximately double number of particles as compared to glucose solution.
   F.P. = 0.1 M KCl < 0.1 M glucose – reason is same.
10. What is meant by Colligative Properties? Give types of colligative properties.
    Ans – The properties of a solution depends upon no of particles of solute not on the nature, in the solution are called colligative properties.
    (a) Relative lowering of vapour pressure (b) Elevation of boiling point (c) Depression of freezing point (d) Osmotic pressure. All are directly proportional to the molality of the solution.

THREE MARKS QUESTIONS

1. Define Osmotic pressure. What do you understand by the term hypertonic and hypotonic solutions? What happens when blood cells are kept in fresh water?
   Ans – Movement of solvent particles through the semipermeable membrane from dilute to concentrate solution is called osmosis.
   The solution which has higher osmotic pressure is called hypertonic whereas the solution which has lower osmotic pressure is called hypotonic solution.
   Blood cells swell because of endosmosis.
2. Given below is the sketch of a plant for carrying out a process.



   (a) Name the process occurring in the above plant.
   (b) To which container does the net flow of solvent take place?
   (c) Give one practical use of the plant.

Ans - (a) Reverse osmosis

(b) To fresh water container

(c) This can be used as a desalination plant to meet potable water requirements.

3. Calculate the boiling point of a solution prepared by adding 15 g of NaCl to 250 g of water. (Kb for water = 0.512 K Kg mol-1 and molar mass of NaCl = 58.5 g/mol). Assuming that NaCl is 100% ionized in water.

Ans - $\Delta Tb = \frac{i \ x \ Kb \ x \ WB \ x \ 1000}{MB \ x \ WA}$

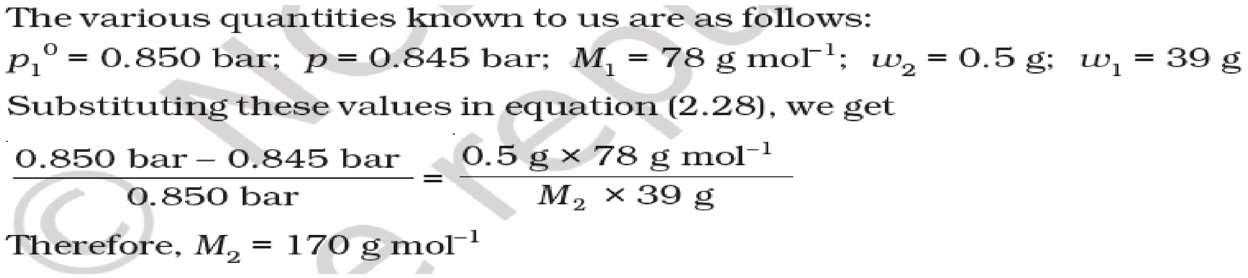
$= \frac{2 \ x \ 0.512 \ x \ 15 \ x \ 1000}{58.5 \ x \ 250}$

= 1.052 K

Boiling point of the solution = 373 + 1.052 = 374.052 K

4. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile solute weighing 0.5 g when added to 39.0 g of benzene (molar mass = 78g/mol). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

Ans -



The various quantities known to us are as follows:

$p_1^0 = 0.850$ bar; $p = 0.845$ bar; $M_1 = 78$ g mol^{-1}; $w_2 = 0.5$ g; $w_1 = 39$ g

Substituting these values in equation (2.28), we get

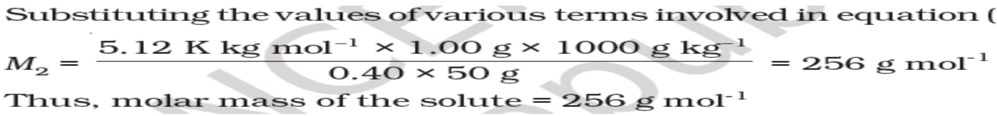
$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

Therefore, $M_2 = 170$ g mol^{-1}

5.

1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute.

Ans –



Substituting the values of various terms involved in equation (2.36) we get,

$$M_2 = \frac{5.12 \text{ K kg mol}^{-1} \times 1.00 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.40 \times 50 \text{ g}} = 256 \text{ g mol}^{-1}$$

Thus, molar mass of the solute = 256 g mol^{-1}

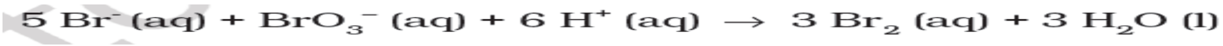
CHEMICAL KINETICS

TWO MARKS QUESTIONS

1. Define the term average rate and instantaneous rate of reaction.

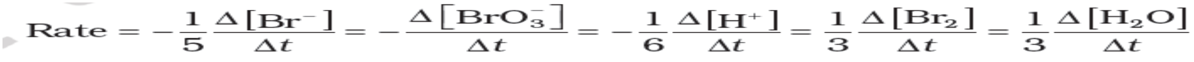
   Ans – Change of concentration of either reactant or product in a measurable time interval is called average rate and if time interval is taken zero then average rate becomes instantaneous rate. Unit of rate = mol/L/s.

2. Write the rate expression with respect to each reactant and product for the reaction given below.



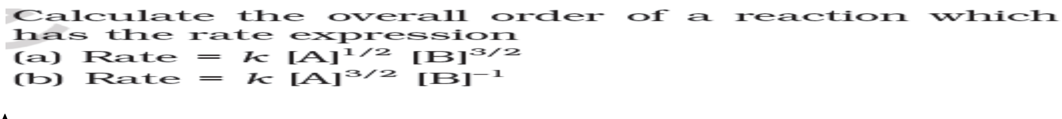
$$5 \text{ Br}^- (aq) + \text{BrO}_3^- (aq) + 6 \text{ H}^+ (aq) \rightarrow 3 \text{ Br}_2 (aq) + 3 \text{ H}_2\text{O} (l)$$

Ans -



$$\text{Rate} = -\frac{1}{5}\frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

3.

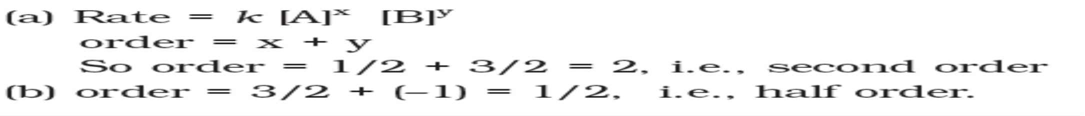


Calculate the overall order of a reaction which has the rate expression

(a) Rate = k [A]$^{1/2}$ [B]$^{3/2}$

(b) Rate = k [A]$^{3/2}$ [B]$^{-1}$

Ans –



(a) Rate = $k\,[A]^x\ [B]^y$

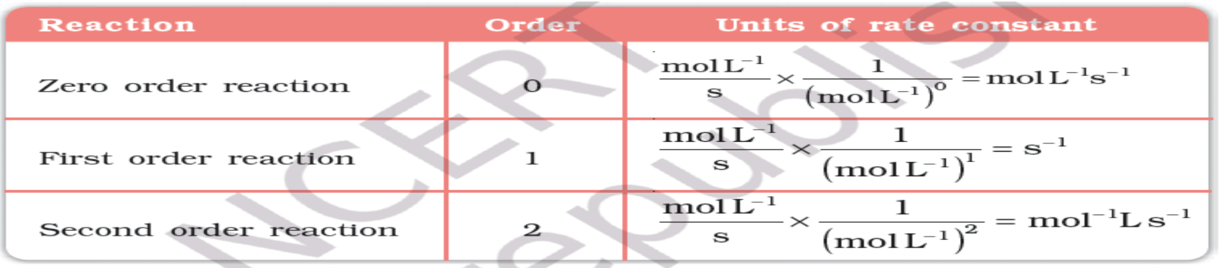
order = $x + y$

So order = $1/2 + 3/2 = 2$, i.e., second order

(b) order = $3/2 + (-1) = 1/2$, i.e., half order.

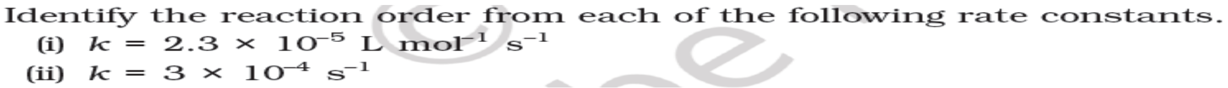
4. What are the units of rate constant for the zero, first and second order of reactions?

Ans –



Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}}\times\frac{1}{(\text{mol L}^{-1})^0}=\text{mol L}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}}\times\frac{1}{(\text{mol L}^{-1})^1}=\text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}}\times\frac{1}{(\text{mol L}^{-1})^2}=\text{mol}^{-1}\text{L s}^{-1}$

5.

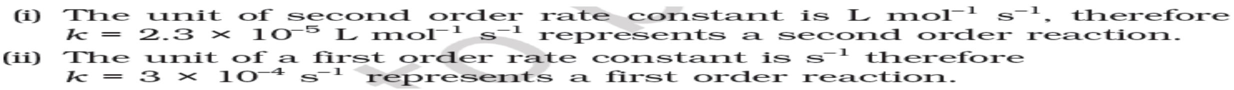


Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

(ii) $k = 3 \times 10^{-4}$ s^{-1}

Ans –

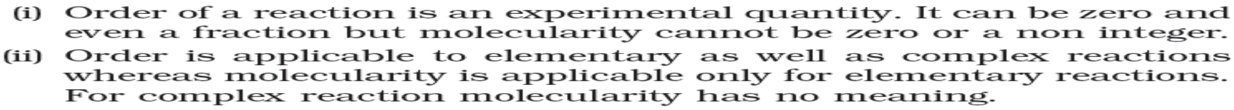


(i) The unit of second order rate constant is L mol^{-1} s^{-1}, therefore $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} represents a second order reaction.

(ii) The unit of a first order rate constant is s^{-1} therefore $k = 3 \times 10^{-4}$ s^{-1} represents a first order reaction.

6. Compare molecularity and order of a reaction.

Ans – OR any two considerable points.



(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

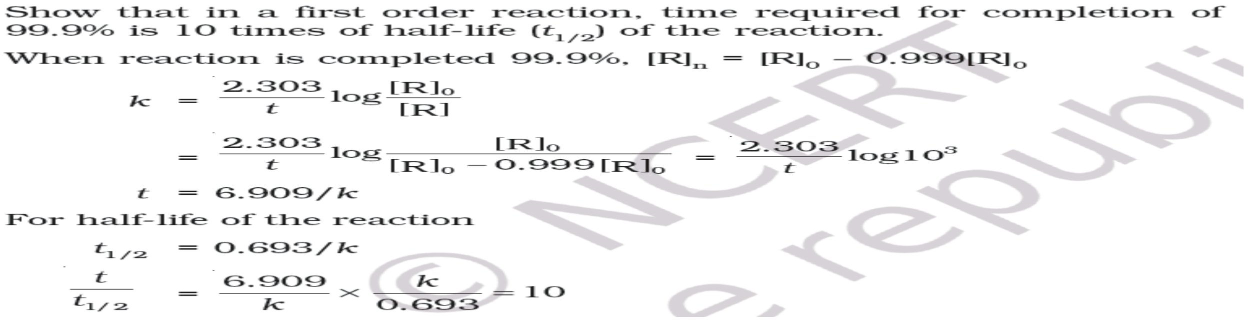
(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

7. Write the integrated rate equations for both zero and first order reactions. Also write their formulas to find half-life.

Ans – For zero order – K = [R]0 – [R]/t & t1/2 = [R]0/2K

For first order – K = 2.303/t . log [R]0/[R] & t1/2 = 0.693/K

8.



Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

When reaction is completed 99.9%, $[R]_n = [R]_0 - 0.999[R]_0$

$$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$$

$$= \frac{2.303}{t}\log\frac{[R]_0}{[R]_0 - 0.999[R]_0} = \frac{2.303}{t}\log 10^3$$

$$t = 6.909/k$$

For half-life of the reaction

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

$$\frac{t}{t_{1/2}} = \frac{6.909}{k}\times\frac{k}{0.693} = 10$$

9. (a) What is the effect of temperature change by 10^{0}C on rate constant?

(b)Define pseudo first order reaction.

Ans – (a) Rate constant becomes doubled.

(b) In a bimolecular reaction, if concentration of one of the reactant is taken in excess, then reaction becomes first order kinetics. Such reactions are known as pseudo first order reactions.

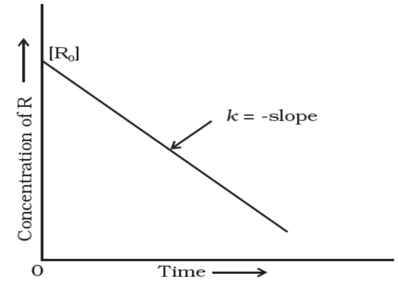
10. Define activation energy. Explain the effect of catalyst on activation energy of a reaction?

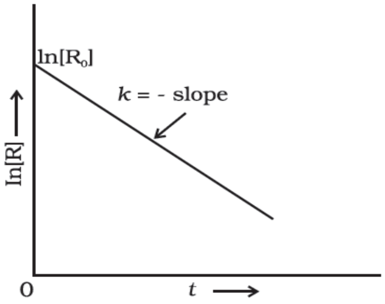
Ans – The minimum amount of energy that is required to cross the energy barrier and form activated complex for the reactant molecules, is called energy of activation.

A catalyst provides an alternate path of lower activation energy and increase the reaction rate.

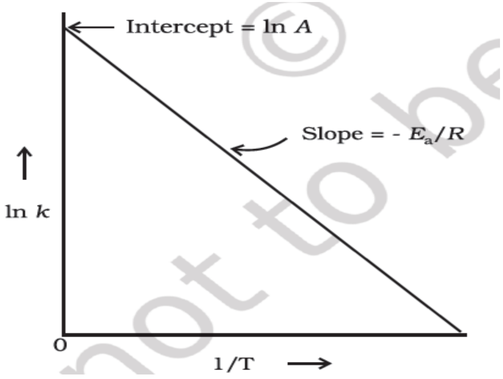
THREE MARKS QUESTIONS

1. Explain the key features of Collision theory.
    i. Collision between the reactant molecules is must.
    ii. Colliding molecules must have proper orientation.
    Iii.Collision frequency must be high.
2. A reaction is first order in A and second order in B.
    (i) Write the differential rate equation.
    (ii) How is the rate affected on increasing the concentration of B three times?
    (iii) How is the rate affected when the concentrations of both A and B are doubled?
    Ans - . (i) Rate = $K[A]^1 [B]^2$
    (ii) Rate = $K[A]^1 [3B]^2 = 9K[A]^1 [B]^2$ hence, it becomes 9 times.
    (iii)Rate = $K[2A]^1 2[B]^2 = 8K[A]^1 [B]^2$ hence, it becomes 8 times.
3. Draw the graphical representations of zero and first order reactions showing time and conc. Of the reactant.





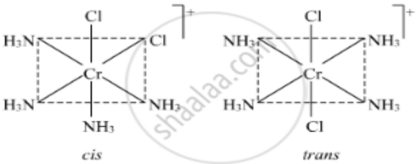
    Ans - (i) zero order (ii) 1st order
4. How is the activation energy of a reaction calculated by graphical method?
    Ans -



    Find the slope and calculate Ea as slope = -Ea/R
5. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.
    (Given: log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK^{-1} mol^{-1})
    Calculate K1 and K2 using two half-lives given and then find Ea.

COORDINATION COMPOUNDS

1. Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex.



Tetraaminedichloridocromium(III) ion.

2. Using IUPAC norms write the formulae for the following :

(a)Pentaamminenitrito-O-cobalt(III) ion
(b)Potassium tetracyanidonickelate(II)

Ans - (i) $[Co(NH_3)_5(ONO)]^{2+}$ (ii) $K_2[Ni(CN)_4]$

3. Define and give one example each of linkage and coordination isomerism.

Ans – Linkage isomerism arises due to presence of ambidentate ligands. Any example

Coordination isomerism arises due to exchange of ligands between positive and negative coordination spheres. Any example.

4. Define ambidentate ligands and chelating ligands with suitable example.

Ans – An ambidentate ligand has two donor sites but monodentate in nature at a time. NO_2^-, SCN^- etc

5. What are homoleptic and heteroleptic complexes?

Ans – In homoleptic complexes all the ligands present are same whereas in heteroleptic complexes different kind of ligands is present. $[Co(NH_3)_6]^{3+}$, , $[Co(NH_3)_4Cl_2]^+$

6. Write the state of hybridisation of central metal and structure of the following complexes- $[NiCl_4]^{2-}$ & $[Ni(CN)_4]^{2-}$

Ans - $[NiCl_4]^{2-}$ is tetrahedral and sp3 hybrid.

$[Ni(CN)_4]^{2-}$ is square planer and dsp2 hybrid.

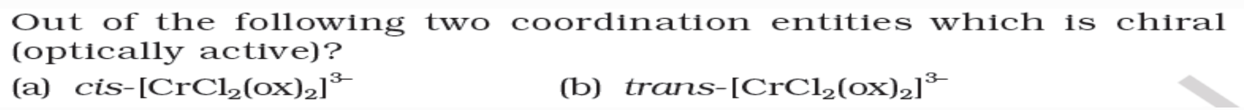
7.

Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Ans -

Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

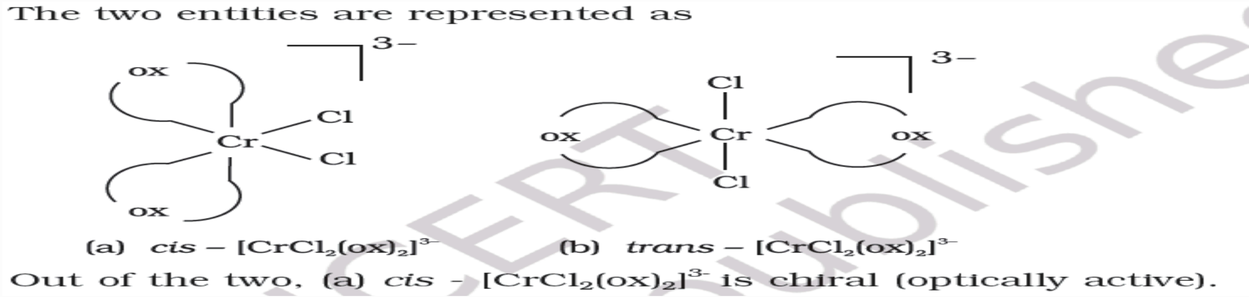
8.



Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

Ans –

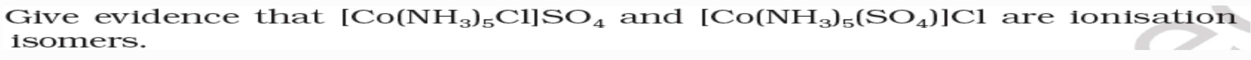


The two entities are represented as

(a) *cis* – $[CrCl_2(ox)_2]^{3-}$ (b) *trans* – $[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) *cis* - $[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

9.



Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.

Ans – first will give white ppt with barium chloride whereas the second will give white ppt with silver nitrate, so these are ionisation isomers.

10. What are the possible hybridisation and geometry of complexes having coordination number 4 and 6?

Ans – Coordination no 4 = dsp2 hybridisation – square planer structure & sp3 hybridisation – tetrahedral structure.

Coordination no 6 = d2sp3 and sp3d2 hybridisation – octahedral structure.

The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion ?

Ans – Since Mn has sp3 hybridisation and 5 unpaired electrons, it has magnetic moment of 5.9 BM.

11.

$[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

Ans – first one has unpaired electrons whereas the second one has no unpaired electron.

12. Complexes with Polydentate ligands are more stable than other complexes. Justify by giving examples.

Ans – Polydentate ligands offer chelating effect which makes the complex more stable.

13. Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory:

$[CoF_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Cu(NH_3)_6]^{2+}$

Ans - $[CoF_6]^{3-}$, $Co^{3+} \rightarrow (3d^6) \rightarrow t_{2g}{}^4 e_g{}^2$

$[Fe(CN)_6]^{4-}$, $Fe^{2+} \rightarrow (3d^6) \rightarrow t_{2g}{}^6 e_g{}^0$

$[Cu(NH_3)_6]^{2+}$,$Cu^{2+} \rightarrow (3d^9) \rightarrow t_{2g}{}^6 e_g{}^3$

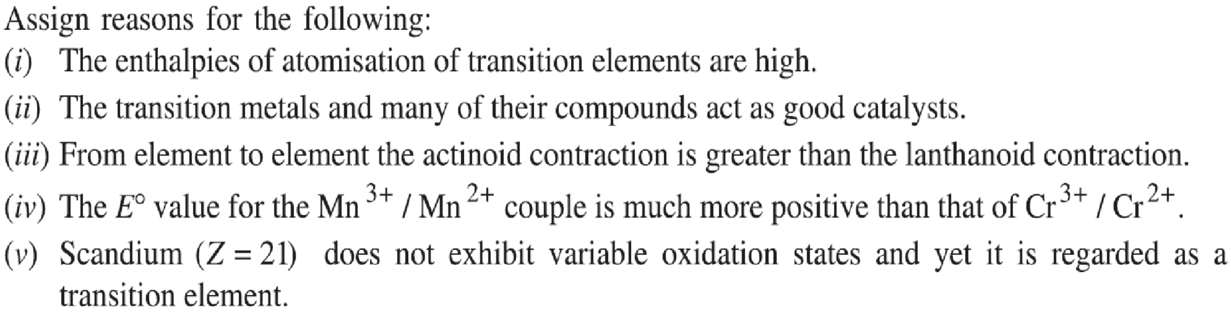
14. Compare the key points of VBT and CFT.

Ans – key points are - VBT is metal centred whereas CFT is ligand centred.

VBT is based of hybridisation hypothesis whereas CFT is based of splitting of d orbitals under the influence of ligands

THE D- AND F-BLOCK ELEMENTS

Q1.



Assign reasons for the following:

(*i*) The enthalpies of atomisation of transition elements are high.

(*ii*) The transition metals and many of their compounds act as good catalysts.

(*iii*) From element to element the actinoid contraction is greater than the lanthanoid contraction.

(*iv*) The E° value for the Mn^{3+} / Mn^{2+} couple is much more positive than that of Cr^{3+} / Cr^{2+}.

(*v*) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element.

Ans-

(*i*) This is because transition metals have strong metallic bonds as they have a large number of unpaired electrons.

(*ii*) The catalytic activity of transition metals is attributed to the following reasons:

- (*a*) Because of their variable oxidation states transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
- (*b*) In some cases, the transition metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

(*iii*) This is due to poorer shielding by $5f$ electrons in actinoids than that by $4f$ electron in the lanthanoids.

(*iv*) This is because half filled d-subshell ($3d^5$) in Mn^{2+} is more stable.

(*v*) This is because scandium has partially filled d orbitals in the ground state ($3d^1 4s^2$).

Q2.

(*a*) What may be the possible oxidation states of the transition metals with the following d electronic configurations in the ground state of their atoms:
$3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$. Indicate relative stability of oxidation states in each case.

(*b*) Write steps involved in the preparation of (i) Na_2CrO_4 from chromite ore and (ii) K_2MnO_4 from pyrolusite ore.

Ans-

(*a*)

Electronic Configuration	Element	Possible O.S.	More stable O.S.
$3d^2 4s^2$	Vanadium	+ 2, + 3, + 4, + 5	+ 5
$3d^5 4s^2$	Manganese	+ 2, + 3, + 4, + 5, + 6, + 7	+ 2, + 7
$3d^6 4s^2$	Iron	+ 2, + 3, + 4, + 6	+ 2, + 3

(*b*) (*i*) Chromite ore is fused with sodium carbonate in excess of air.

$$\underset{\text{Chromite ore}}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{\text{Sod. chromate}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

(*ii*) Pyrolusite ore (MnO_2) is fused with KOH in the presence of O_2 or oxidising agent such as KNO_3.

$$\underset{\text{Pyrolusite ore}}{2MnO_2} + 4KOH + O_2 \longrightarrow \underset{\text{Potassium maganate}}{2K_2MnO_4} + 2H_2O$$

Q3.

Discuss the relative stability in aqueous solutions of +2 oxidation state among the elements : Cr, Mn, Fe and Co. How would you justify this situation?
(At. Nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

Ans-

On the basis of electrochemical series the standard electrode potential shows the following order

$$E^\circ_{Mn^{2+}/Mn} < E^\circ_{Cr^{2+}/Cr} < E^\circ_{Fe^{2+}/Fe} < E^\circ_{Co^{2+}/Co}$$

Therefore, Co^{2+} gets easily reduced to metallic cobalt while it is difficult to reduce Mn^{2+}. Hence Mn^{2+} will be most stable and the increasing stability order will be

$$Co^{2+} < Fe^{2+} < Cr^{2+} < Mn^{2+}$$

Q4.

Compare actinoids and lanthanoids with reference to their :

(*i*) electronic configurations of atoms

(*ii*) oxidation states of elements

(*iii*) general chemical reactivity of elements.

Ans-

	Characteristics	Lanthanoids	Actinoids
(*i*)	Electronic configuration	[Xe] $4f^{-14} 5d^{0-1} 6s^2$	[Rn] $5f^{1-14} 6d^{0-1} 7s^2$
(*ii*)	Oxidation states	Besides +3 O.S.Lanthanoids show +2 and +3 O.s. only in a few cases.	Besides +3 o.s. actinoids show higher o.s. of +4, +5, +6, +7 also because of smaller energy gap between $5f$, $6d$ and $7s$ subshell.
(*iii*)	General chemical reactivity of elements	These are less reactive metals	These are highly reactive metals.
		Lesser tendency towards complex formation.	Greater tendency towards complex formation.
		Do not form oxocation	Form oxocation
		Compounds are less basic.	Compounds are more basic.

Q5.

Assign a reason for each of the following:

(*i*) The third ionization energy of Mn ($Z = 25$) is higher than that of either Cr ($Z = 24$) or Fe ($Z = 26$).

(*ii*) Simple copper (I) salts are not stable in aqueous solutions.

Ans-

(*i*) This is because Mn^{2+} is more stable as it has exactly half filled configuration $3d^5 4s^0$.

(*ii*) Cu^{2+} (aq) is much more stable than Cu^+ (aq). This is because, although second ionization enthalpy of copper is large but for Cu^{2+} (aq) is much more negative than that of Cu^+ (aq) and therefore, it more than compensates for the second ionisation enthalpy of copper. Therefore, Cu^+ ion aqueous solution undergoes disproportionation.

$$2Cu^{2+} (aq) \longrightarrow Cu^{2+} (aq) + Cu(s)$$

Q6.

Describe the trends in the following properties of the first series of the transition elements :

(*i*) Oxidation states

(*ii*) Atomic sizes

(*iii*) Magnetic behaviour of dipositive gaseous ions (M^{2+})

Ans-

(*i*) As there is very little energy difference between 4*s* and 3*d* orbitals, electrons from both energy levels can be used for chemical bond formation. Therefore all elements except Sc and Zn, of the first transition series show a number of oxidation states as shown in table.

Oxidation states of the first series transition elements (the most common ones are in bold letter)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	
+3	+3	+3	+3	+3	**+3**	**+3**	+3	**+2**	**+2**
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

(*ii*) Atomic radii of the first transition series decreases from Sc to Cr, then remains almost constant till Ni and then increases from Cu to Zn.

The reason of this variation in atomic radii has been attributed to the increase in nuclear charge in the beginning of the series. But as the electrons continue to be filled in *d*-orbitals, they screen the outer 4*s* electrons from the influence of nuclear charge. When the increased nuclear charge and the increased screening effect balance each other in the middle of transition series, the atomic radii becomes almost constant (Mn to Fe). Towards the end of the series, the repulsive interaction between electrons in *d* orbitals become very dominant. As a result there is an expension of the electron cloud; consequently, the atomic size increases.

(*iii*) Except Zn^{2+}, all other divalent gaseous ions of the first series of the transition elements contain unpaired electrons in their 3*d* subshell and are therefore paramagnetic in nature.

The magnetic moment (μ) of the elements of the first transition series can be calculated with the unpaired electrons (*n*) by the spin-only formula

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

Ion	Configuration	Unpaired electrons	Magnetic moment (μ) calculated
Mn^{2+}	$3d^5 4s^0$	5	$\sqrt{5(5+2)} = 5.92$ B.M.
Cu^{2+}	$3d^9 4s^0$	1	$\sqrt{1(1+2)} = 1.73$ B.M.
Zn^{2+}	$3d^{10} 4s^0$	0	$\sqrt{0(0+3)} = 0$

Q7.

(*a*) Complete the following chemical reaction equations: **5**

(*i*) $MnO_{4(aq)}^{-} + C_2O_{4\,(aq)}^{2-} + H^{+}(aq) \longrightarrow$

(*ii*) $Cr_2O_{7(aq)}^{2-} + F^{2+}(aq) + H^{+}(aq) \longrightarrow$

(*b*) Explain the following observations about the transition/inner transition elements:

(*i*) There is in general an increase in density of element from titanium (Z = 22) to copper (Z = 29).

(*ii*) There occurs much more frequent metal-metal bonding in compounds of heavy transition elements (3rd series).

(*iii*) The members in the actinoid series exhibit a large number of oxidation states than the corresponding members in the lanthanoid series.

Ans-

(*a*) (*i*) In acidic medium:

$$\mathrm{Mn\ O_4^- + 8H^+ + 5\bar{e} \longrightarrow Mn^{2+} + 4H_2O] \times 2}$$

$$\mathrm{C_2O_4^{2-} \longrightarrow 2CO_2 + 2\bar{e}\,] \times 5}$$

$$\mathrm{2Mn\ O_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2M_n^{2+} + 10CO_2 + 8H_2O}$$

(*ii*) In acidic medium:

$$\mathrm{Cr_2\ O_7^{2-} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{3+} + 7H_2O}$$

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + \bar{e}\,] \times 6}$$

$$\mathrm{Cr_2\ O_7^{2-} + 6Fc^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fc^{3+} + 7H_2O}$$

Q8.

(*a*) Complete the following chemical equations for reactions:

(*i*) $\mathrm{MnO_4^-{}_{(aq)} + S_2O_3^{2-}{}_{(aq)} + H_2O_{(l)} \longrightarrow}$

(*ii*) $\mathrm{CrO_7^-{}_{(aq)} + H_2S_{(g)} + H^+{}_{(aq)} \longrightarrow}$

(*b*) Give an explanation for each of the following observations:

(*i*) The gradual decrease in size (actinoid contraction) from element to element is greater among the actinoids than that among the lanthanoids (lanthanoid contraction).

(*ii*) The greatest number of oxidation states are exhibited by the members in the middle of a transition series.

(*iii*) With the same *d*-orbital configuration (d^4) $\mathrm{Cr^{2+}}$ ion is a reducing agent but $\mathrm{Mn^{3+}}$ ion is an oxidising agent.

Ans-

(*a*) (*i*) In neutral or faintly alkaline solutions

$$\mathrm{MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 2H_2O + 4\bar{O}H\,] \times 8}$$

$$\mathrm{S_2O_3^{2-} + 10\bar{O}H \longrightarrow 2\,SO_4^{2-} + 5\,H_2O + 8e^-\,] \times 3}$$

$$\mathrm{8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2\bar{O}H}$$

(*ii*) In acidic solutions

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O}$$

$$\mathrm{H_2S \longrightarrow S + 2H^+ + 2e^-\,] \times 3}$$

$$\mathrm{Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O}$$

(*b*) (*i*) This is due to poor shielding by 5*f* electrons from element to element in actinoids than by 4*f* electrons in lanthanoid series.

(*ii*) This is due to involvement of both $(n-1)\,d$ and *ns* electrons in bonding, which are unpaired in maximum number at the middle of series.

(*iii*) $\mathrm{Cr^{2+}}$ has the configuration d^4 and easily changes to $\mathrm{Cr^{3+}}$ which has half t_{2g} configuration and hence move stable. Therefore $\mathrm{Cr^{2+}}$ is reducing. On the other hand, the change from $\mathrm{Mn^{3+}}$ to $\mathrm{Mn^{2+}}$ results in the half filled, d^5 configuration which has extra stability. Therefore $\mathrm{Mn^{3+}}$ is oxidising.

Q9.

(*a*) Complete the following chemical reaction equations:

(*i*) $\mathrm{Fe^{2+}{}_{(aq)}\ MnO_{4(aq)}^- + H^+{}_{(aq)} \longrightarrow}$

(*ii*) $\mathrm{Cr_2O_{7(aq)}^{2-} + I^-{}_{(aq)} + H^+{}_{(aq)} \longrightarrow}$

(*b*) Explain the following observations:

(*i*) Transition elements are known to form many interstitial compounds.

(*ii*) With the same d^4 *d*-orbital configuration $\mathrm{Cr^{2+}}$ ion is reducing while $\mathrm{Mn^{3+}}$ ion is oxidising.

(*iii*) The enthalpies of atomisation of the transition elements are quite high.

Ans-

(*a*) (*i*)

$$\begin{array}{rcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^-] \times 5 \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ & \longrightarrow & Mn^{2+} + 5Fe^{3+} + 4H_2O \\ \hline \end{array}$$

(*ii*)

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ 2I^- & \longrightarrow & I_2 + 2e^-] \times 3 \\ \hline Cr_2O_7^{2-} + 6I^- + 14H^+ & \longrightarrow & 2Cr^{3+} + 3I_2 + 7H_2O \\ \hline \end{array}$$

(*b*) (*i*) Transition elements form many interstitial compounds as they are capable of entrapping small atoms like H, C or N in the interstitial sites in their crystal lattice.

(*ii*) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half filled t_{2g} configuration. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled d^5 configuration which has extra stability therefore Mn^{3+} is oxidising.

(*iii*) This is because transition metals have strong metallic bonds as they have a large number of unpaired electrons.

Q10.

(*a*) Complete the following chemical reaction equations:

(*i*) $CrO_7^{2-}{}_{(aq)} + H_2S_{(g)} + H^+{}_{(aq)} \longrightarrow$

(*ii*) $MnO_{2(s)} + KOH_{(aq)} + O_{(2)} \longrightarrow$

(*b*) Explain the following observations:

(*i*) Transition metals form compounds which are usually coloured.

(*ii*) Transition metals exhibit variable oxidation states.

(*iii*) The actinoids exhibit a greater range of oxidation states than the lanthanoids.

Ans-

(*a*) (*i*)

$$\begin{array}{rcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ H_2S & \longrightarrow & S + 2H^+ + 2e^-] \times 3 \\ \hline Cr_2O_7^{2-} + 3H_2S + 8H^+ & \longrightarrow & 2Cr^{3+} + 3S + 7H_2O \\ \hline \end{array}$$

(*ii*) $$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

(*b*) (*i*) This is due to $d-d$ transition as the energy of excitation of d orbital electrons from lower energy to higher energy level lies in the visible region.

(*ii*) The variable oxidation states of transition metals are due to the participation of *ns* and $(n-1)d$ electrons in bonding as energy difference between ns and $(n-1)d$ orbitals is small.

(*iii*) This is due to comparable energies of $5f$, $6d$ and $7s$ orbitals of actinoids.

Q11.

(*a*) Complete the following chemical reaction equations:

(*i*) $Cr_2O_7^{2-}{}_{(aq)} + I^-{}_{(aq)} + H^+{}_{(aq)} \longrightarrow$

(*ii*) $MnO_4^-{}_{(aq)} + Fe^{2+}{}_{(aq)} + H^+{}_{(aq)} \longrightarrow$

(*b*) Explain the following observations:

(*i*) In general the atomic radii of transition elements decrease with atomic number in a given series.

(*ii*) The $E^o_{M^{2+}|M}$ for copper is positive (+ 0.34 V). It is the only metal in the first series of transition elements showing this type of behaviour.

(*iii*) The E^o value for $Mn^{3+} | Mn^{2+}$ couple is much more positive than for $Cr^{3+} | Cr^{2+}$ or $Fe^{3+} | Fe^{2+}$ couple.

Ans-

(*a*) (*i*)

$$\begin{array}{lcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ 2I^- & \longrightarrow & I_2 + 2e^-] \times 3 \\ \hline Cr_2O_7^{2-} + 6I^- + 14H^+ & \longrightarrow & 2Cr^{3+} + 3I_2 + 7H_2O \\ \hline \end{array}$$

(*ii*)

$$\begin{array}{lcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^-] \times 5 \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ & \longrightarrow & Mn^{2+} + 5Fe^{3+} + 4H_2O \\ \hline \end{array}$$

(*b*) (*i*) The atomic radii of transition metals decreases with atomic number in a series as the nuclear change increases due to poor shielding effect of d orbitals.

(*ii*) This is due to its high enthalpy of atomization and low hydration enthalpy.

(*iii*) This is due to much large third ionisation energy of Mn as Mn^{2+} is very stable on account of stable d^5 configuration.

Q12.

Complete the following chemical reaction equations:

(*i*) $MnO_4^-(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(*ii*) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Ans-

(*i*)

$$\begin{array}{lcl} MnO_4^- + 8H^+ + 5e^- & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2e^-] \times 5 \\ \hline 2MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 10CO_2 + 8H_2O \\ \hline \end{array}$$

(*ii*)

$$\begin{array}{lcl} Cr_2O_7^{2-} + 14H^+ + 6e^- & \longrightarrow & 2Cr^{3+} + 7H_2O \\ Fe^{2+} & \longrightarrow & Fe^{3+} + e^-] \times 6 \\ \hline Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ & \longrightarrow & 2Cr^{3+} + 6Fe^{3+} + 7H_2O \\ \hline \end{array}$$

Q13.

(*a*) What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

(*b*) Explain the following observations:

(*i*) Cu^+ ion is unstable in aqueous solutions.

(*ii*) Although Co^{2+} ion appears to be stable, it is easily oxidised to Co^{3+} ion in the presence of a strong ligand.

(*iii*) The $E^0_{Mn^{2+}|Mn}$ value for manganese is much more than expected from the trend for other elements in the series.

Ans-

(*a*) **Lanthanoid contraction:** The steady decrease in the atomic and ionic radii of lanthanoids with increase in atomic number is known as lanthanoid contraction.

Cause of lanthanoid contraction: As we move along the lanthanoid series, for every additional proton in the nucleus, the corresponding electron goes into 4*f*–subshell, there is poor shielding of one electron by another in this subshell due to the shapes of these *f*-orbitals. The imperfect shielding is not able to counterbalance the effect of the increased nuclear charge. Thus the net result is decrease in size with increase in atomic number.

Consequences:

(*i*) 5*d* series elements have nearly same radii as that of 4*d*-series.

(*ii*) The basic strength of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

(*b*) (*i*) Because the high hydration enthalpy of Cu^{2+} easily compensates the second ionization enthalpy of Cu.

(*ii*) Because strong ligand cause spin pairing giving rise to diamagnetic octahedral complex which are very stable and have very large crystalfield stabilization energy. This splitting energy overcomes the ionization enthalpy.

(*iii*) This is due to stability of Mn^{2+} as it has half filled d^5 configuration.

Q14.

How would you account for the following: **3**

(*i*) Many of the transition elements and their compounds can act as good catalysts.

(*ii*) The metallic radii of the third (5*d*) series of transition elements are virtually the same as those of the corresponding members of the second series.

(*iii*) There is a greater range of oxidation states among the actinoids than among the lanthanoids.

Ans-

(*i*) The catalytic activity of transition metals is attributed to the following reasons:

(a) Because of their variable oxidation states transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.

(*b*) In some cases, the transition metal provides a suitable large surface area with free vacancies on which reactants are adsorbed.

(*ii*) This due to filling of 4*f* orbitals which have poor shielding effect or due to lanthanoid contraction.

(*iii*) This is due to comparable energies of 5*f*, 6*d* and 7*s* orbital in actinoids.

Q15.

State reasons for the following observations: **2**

(*i*) The enthalpies of atomisation of transition elements are quite high.

(*ii*) There is a greater horizontal similarity in the properties of the transition elements than of the main group elements.

Ans-

(*i*) This is because, transition elements have strong metallic bonds due to presence of large number of unpaired electrons.

(*ii*) This is because in transition elements incoming electron goes into d-orbitals of inner shell whereas in main group elements, the incoming electron goes to outermost shell.

Q16.

Explain the following observations: **3**

(*i*) With the same d-orbital configuration (d^4) Cr^{2+} ion is a reducing agent while Mn^{3+} ion is an oxidising agent.

(*ii*) Cu^+ ion is not stable in aqueous solutions.

(*iii*) Among the 3*d* series of transition elements, the largest number of oxidation states are exhibited by manganese.

Ans-

(*i*) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half filled t_{2g} configuration. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled d^5 configuration which has extra stability therefore Mn^{3+} is oxidising.

(*ii*) Because the high hydration enthalpy of Cu^{2+} easily compensates the second ionization enthalpy of Cu.

(*iii*) This is because manganese has electronic configuration $[Ar]3d^5 4s^2$, with five unpaired electrons in 3*d* orbitals.

Q17.

Explain the following observations:

(*i*) Generally there is an increase in density of elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements.

(*ii*) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.

Ans-

(*i*) The density of elements from titanium to copper increase in the first series of transition elements. This is due to decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density.

(*ii*) Many transition metals and their components show catalytic properties. This property is due to their ability to exhibit variable oxidation states (incomplete d-orbitals) which enable them to form unstable intermediates.

Q18.

Complete the following chemical equations:

(*i*) $C_2O_7^{2-}(aq) + C_2O_4^{2-}(aq) + H^+(aq) \longrightarrow$

(*ii*) $MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

Ans-

(*i*) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6\bar{e} \longrightarrow 2Cr^{3+}(aq) + 7H_2O$

$C_2O_4^{2-}(aq) \longrightarrow 2CO_2 + 2\bar{e}] \times 3$

$\underline{Cr_2O_7^{2-}(aq) + 3(C_2O_4^{2-}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6CO_2 + 7H_2O}$

(*ii*) $MnO_4^-(aq) + 8H^+(aq) + 5\bar{e} \longrightarrow Mn^{2+}(aq) + 4H_2O$

$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + \bar{e}] \times 5$

$\underline{MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O}$

Q19.

How would you account for the following?

(*i*) The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) series.

(*ii*) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.

(*iii*) The highest oxidation state of a metal is exhibited in its oxide or fluoride.

Ans-

(*i*) This is due to lanthanide contraction.

or

This is due to filling of 4*f* orbitals which have poor shielding effect.

(*ii*) The E° value for the Mn^{3+}/Mn^{2+} couple is much positive than Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple because Mn^{3+} ion receiving an electron gets d-subshell half-filled which is highly stable. While in case of Fe^{3+} d-sub shell is already half-filled, so it does not receive electron easily.

(*iii*) This is because fluorine and oxygen are highly electronegative elements and have small size.

Q20.

Explain the following observations:

(*i*) Transition elements generally form coloured compounds.

(*ii*) Zinc is not regarded as a transition element.

Ans-

(*i*) This is due to d-d transition. When visible (white) light falls on a compound, it absorbs certain radiations of white light and transmit the remaining ones. The transmitted light has the complementary colour to that of the absorbed light.

(*ii*) Because the atoms or simple ions of zinc never have partially filled d orbitals.

Q21.

(*a*) Complete the following chemical equations:

(*i*) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+(aq) \longrightarrow$

(*ii*) $Cu^{2+}(aq) + I^-(aq) \longrightarrow$

(*b*) How would you account for the following:

(*i*) The oxidising power of oxoanions are in the order $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.

(*ii*) The third ionization enthalpy of manganese (Z = 25) is exceptionally high.

(*iii*) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

Ans-

(*a*) (*i*) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$

(*ii*) $2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$

(*b*) (*i*) The oxidising power of oxonions are in the order $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$, this is due to increase in the oxidation state of the metal ion.

(*ii*) The third ionisation enthalpy of manganese (Z = 25) is exceptionally high because Mn^{2+} ion has $3d^5$ configuration which is highly stable since it is half-filled.

(*iii*) Cr^{2+} stronger reducing agent than Fe^{2+} as its configuration changes from d^4 to d^3, a more stable half filled t_{2g} configuration.

Q22.

(*a*) Complete the following chemical equations:

(*i*) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \longrightarrow$

(*ii*) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow$

(*b*) Explain the following observations:

(*i*) La^{3+} (Z = 57) and Lu^{3+} (Z = 71) do not show any colour in solutions.

(*ii*) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.

(*iii*) Cu^+ ion is not known in aqueous solutions.

Ans-

(*a*) (*i*) $8MnO_4^-(aq) + 3S_2O_3^{2-}(aq) + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(*ii*) $Cr_2O7(aq) + 6Fe^{2+}(aq) + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$

(*b*) (*i*) La^{3+} and Lu^{3+} ions do not show any colour in solution because they do not contain any unpaired electrons.

(*ii*) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism because manganese (Mn^{2+}) ion has maximum number of 5 unpaired electrons.

(*iii*) Cu^+ ion is not known in aqueous solutions because Cu^{2+} ions are more stable due to more negative ΔH_{hyd} of Cu^{2+} than Cu^+, which is more than compensates for the second ionisation enthalpy of Cu.

Q23.

Describe the preparation of

(*i*) Potassium dichromate from sodium chromate, and

(*ii*) $KMnO_4$ from K_2MnO_4

Ans-

(*i*) Preparation of potassium dichromate from sodium chromate

(*a*) $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2CrO_7 + Na_2SO_4 + H_2O$

(*b*) $Na_2CrO_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

(*ii*) Preparation of $KMnO_4$ from K_2MnO_4

$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$

OR

$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$

Q24.

Explain the following observations:

(*i*) The enthalpies of atomisation of transition metals are quite high.

(*ii*) There is a close similarity in physical and chemical properties of the 4 d and 5 d series of the transition elements, much more than expected on the basis of usual family relationship.

(*iii*) The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series.

Ans-

(*i*) This is because transition metals have strong metallic bonds as they have large number of unpaired electrons.

(*ii*) There is a close similarity in physical and chemical properties of the 4*d* and 5*d* series of the transition elements much more than expected on the basis of usual family relationship. This is because 5*d* and 4*d* series elements have virtually the same atomic and ionic radii due to lanthanide contraction. Due to equality in size of Zr and Hf, Nb and Ta, Mo and W, etc., the two elements of pair have the same properties.

(*iii*) The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanide series due to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies.

Q25.

Explain the following:

(*i*) The transition elements have great tendency for complex formation.

(*ii*) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers.

(*iii*) Lanthanum and Lutetium do not show colouration in solutions. (At. No.: La = 57, Lu = 71)

Ans-

(*i*) The transition elements have great tendency for complex formation due to presence of vacant d-orbitals of suitable energy, small size of cations and higher nuclear charge.

(*ii*) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers due to poor shielding effect of d-electrons, the net electrostatic attraction between the nucleus and the outermost electrons increase.

(*iii*) Lanthanum and Lutetium do not show colouration in solutions because both the element exhibit +3 oxidation state in their compound thus their cations do not possess any unpaired electrons in them.

Q26.

Assign reasons for the following :

(*i*) Copper (I) ion is not known in aqueous solution.

(*ii*) Actinoids exhibit greater range of oxidation states than lanthanoids.

Ans-

(*i*) In aqueous solution Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

$$2\,Cu^+\,(aq) \longrightarrow 2\,Cu^{2+}(aq) + Cu(s)$$

The higher stability of Cu^{2+} in aqueous solution may be attributed to its greater negative $\Delta_{hyd}H^\circ$ than that of Cu^+. It compensates the second ionization enthalpy of Cu involved in the formation of Cu^{2+} ions.

(*ii*) Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f* and 6*d* orbitals belonging to actinoids than the energy difference between 4*f* and 5*d* orbitals in case of lanthanoids.

Q27.

Complete the following chemical equations:

(*i*) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow$

(*ii*) $KMnO_4 \xrightarrow{\text{heated}}$

(*iii*) $Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow$

Ans-

(*i*)

$$\begin{array}{lcl} MnO_4^- + 8H^+ + 5\bar{e} & \longrightarrow & Mn^{2+} + 4H_2O] \times 2 \\ C_2O_4^{2-} & \longrightarrow & 2CO_2 + 2\bar{e}\ ] \times 5 \\ \hline 2MnO_4^- + 5C_2O_4^{2-} + 16H^+ & \longrightarrow & 2Mn^{2+} + 10CO_2 + 8H_2O \\ \hline \end{array}$$

(*ii*) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$

(*iii*)

$$\begin{array}{lcl} Cr_2O_7^{2-} + 14H^+ + 6\bar{e} & \longrightarrow & 2Cr^{3+} + 7H_2O \\ H_2S & \longrightarrow & 2H^+ + S + 2e] \times 3 \\ \hline Cr_2O_7^{2-} + 3H_2S + 8H^+ & \longrightarrow & 2Cr^{3+} + 3S + 7H_2O \\ \hline \end{array}$$

Q28.

Assign reasons for each of the following:

(*i*) Transition metals generally form coloured compounds.

(*ii*) Manganese exhibits the highest oxidation state of +7 among the 3*d* series of transition elements.

Ans-

(*i*) This is due to *d-d* transition. When visible (white) light falls on a transition metal compounds, they absorb certain radiation of visible light and transmit the remaining ones. The colour observed corresponds to complementary colour of the light absorbed.

(*ii*) As manganese has maximum number of unpaired electrons (5) in 3*d* subshell in addition to 2 electrons in the 4*s* subshell.

Q29.

What is meant by 'lanthanoid contraction'?

Ans-

The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number as we move across the series from lanthanum to lutetium is known as lanthanoid contraction.

Q30.

How would you account for the following:

(*i*) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{3+} is an oxidising agent.

(*ii*) In a transition series of metals, the metal which exhibits the greatest number of oxidation occurs in the middle of the series.

Ans-

(*i*) Cr^{2+} is reducing as its configuration changes from d^4 to d^3, a more stable half filled t_{2g} configuration while Mn^{3+} is oxidising as Mn^{3+} to Mn^{2+}results a more stable half filled d^5 configuration.

(*ii*) It is due to greater number of unpaired electrons in $(n-1)d$ and ns orbitals at the middle of the series.

AMINES

Q1.

Account for the following observations:

(*i*) pK_b for aniline is more than that for methylamine.

(*ii*) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

(*iii*) Aniline does not undergo Friedel-Crafts reaction.

Ans-

(*i*) In aniline due to resonance the lone pair of electrons on the nitrogen atom are delocalized over the benzene ring. As a result, the electron density on the nitrogen decreases. On the other hand, in methyl amine +I effect of CH_3 increases the electron density on the nitrogen atom. Therefore aniline is a weaker base than methyl amine and hence its pK_b value is higher than that of methyl amine.

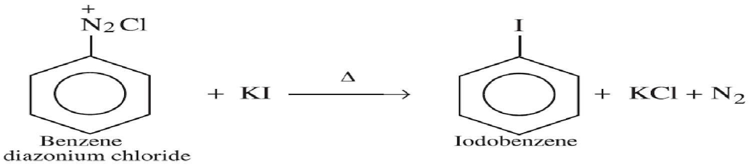
(*ii*) $$CH_3-NH_2 + H_2O \rightleftharpoons CH_3\overset{+}{N}H_3 + \overline{O}H$$

Due to alkaline nature of solution of methylamine precipitation of $Fe(OH)_3$ occurs.

$$FeCl_3 + 3\overline{O}H \longrightarrow \underset{\text{(Brown ppt)}}{\underset{\text{Ferric hydroxide}}{Fe(OH)_3}} \downarrow + 3Cl^-$$

(*iii*) Aniline being a Lewis base, reacts with lewis acid $AlCl_3$ to form a salt. Due to this N atom of aniline acquires positive charge and hence acts as a strong deactivation group for further reaction.

Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.



Q2.

Why do amines behave as nucleophiles?

Ans- Due to the presence of a lone pair of electrons on nitrogen atom.

Q3.

Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions: **1**

NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$

Ans-

$NH_3 < (CH_3)_3N < CH_3-NH_2 < (CH_3)_2NH$.

Q3.

Give the IUPAC name of $H_2N - CH_2 - CH_2 - CH = CH_2$.

Ans- But-3-en-1-amine.

Q4.

Why is an alkylamine more basic than ammonia?

Ans-

Alkyl amine is more basic than ammonia because the + I effect or electron donating nature of alkyl group increases electron density on 'N' atom in alkyl amine.

Q5.

Account for the following :

(*i*) pK_b of methylamine is less than that of aniline.

(*ii*) Aniline does not undergo Friedel–Crafts reaction.

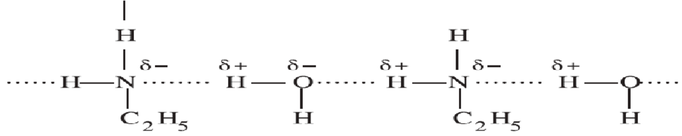
(*iii*) Ethylamine is freely soluble in water whereas aniline is only slightly soluble.

Ans-

(*i*) In aniline, due to resonance, the lone pair of electrons on the nitrogen atom are delocalized over the benzene ring. As a result, the electron density on the nitrogen decreases. On the other hand, in methyl amine +ve I effect of CH_3 increases the electrondensity on the nitrogen atom. Therefore aniline is a weaker base than methyl amine and hence its pK_b value is higher than that of methyl amine.

(*ii*) Aniline being a Lewis base reacts with lewis acid $AlCl_3$ to form a salt. Due to this, N atom of aniline acquires positive charge and hence acts as a strong deactivation group for further reaction.

(*iii*) Ethyl amine is freely soluble in water because it forms hydrogen bonds with water molecules.



On the other hand in aniline to large, hydrocarbon part, the extent of hydrogen bonding decreases considerably and hence aniline is slightly soluble.

Q6.

Why is methylamine more basic than aniline?

Ans-

Methylamine is more basic than aniline due to resonance in aniline and lower stability of aniline ions.

Q7.

Ethylamine is soluble in water whereas aniline is almost insoluble. Why?

Ans-

Due to hydrogen bonding ability of ethylamine.

Q8.

Why are diazonium salts of aromatic amines more stable than those of aliphatic amines?

Ans-

The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring.

Q9.

Giving an example for each, describe the following reactions:

(*i*) Hofmann's bromamide reaction

(*ii*) Gatterman reaction

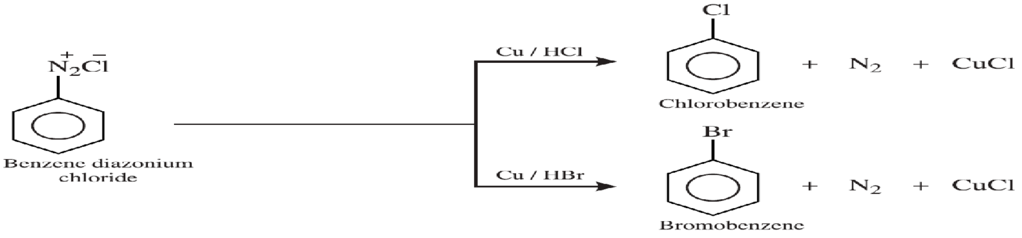
(*iii*) A coupling reaction

Ans-

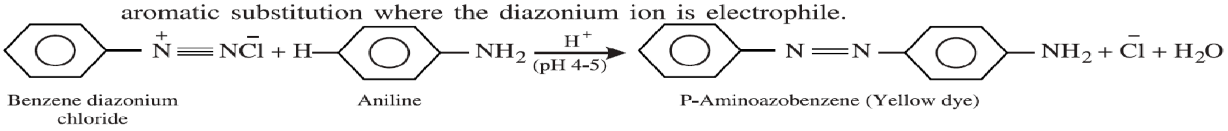
(*i*) **Hoffman's bromamide reaction:** When a primary acidamide is heated with bromine in an aqueous or ethanolic solution of sodium hydroxide, it gives a primary amine with one carbon atom less. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.

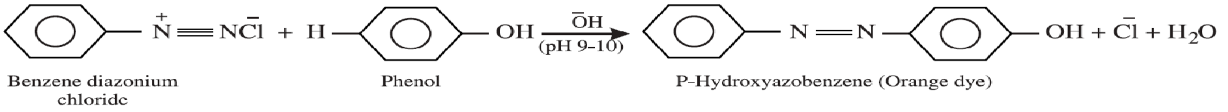
$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

(*ii*) **Gattermann reaction:** Chlorine or bromine can be introduced in benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.



(*iii*) **Coupling reaction:** Diagonium salts react with aromatic amines in weakly acidic medium and with phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at para position of amines or phenols. The mechanism is basically that of electrophilic aromatic substitution where the diazonium ion is electrophile.





Q10.

Complete the following reaction equations:

(*i*) $C_6H_5N_2Cl + CH_3COCl \longrightarrow$

(*ii*) $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow$

(*iii*) $C_2H_5NH_2 + HNO_2 \longrightarrow$

Ans-

(*i*)

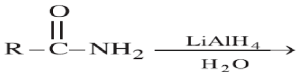
(*ii*) $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHC_2H_5$

(*iii*) $C_2H_5-NH_2 + HNO_2 \longrightarrow C_2H_5-OH + H_2O + N_2$

Q11.

Complete the following reaction equations:

(*i*)



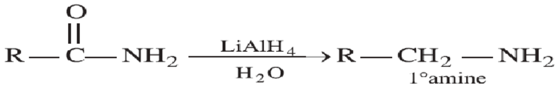
$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4}$

(*ii*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(*iii*) $C_6H_5NH_2 + Br_2\ (aq) \longrightarrow$

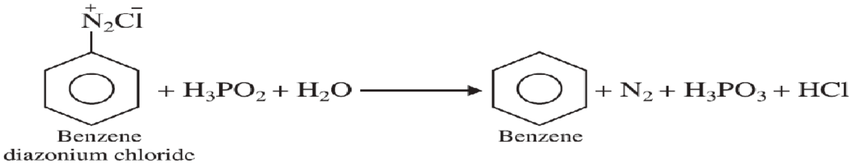
Ans-

(*i*)



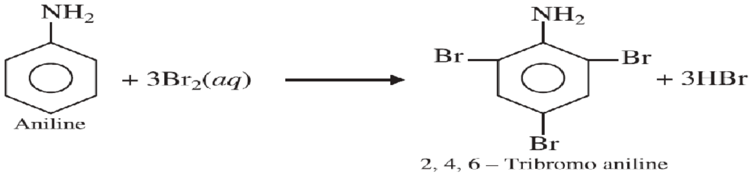
$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4} \underset{1°\text{amine}}{R-CH_2-NH_2}$

(*ii*)



Benzene diazonium chloride

Benzene



Aniline

2, 4, 6 – Tribromo aniline

Q12.

How are the following conversions carried out:

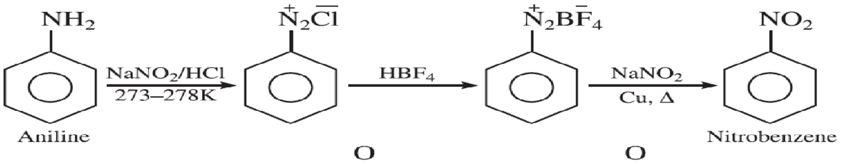
(*i*) Aniline to nitrobenzene

(*ii*) Ethanamine to N-ethylethanamide

(*iii*) Chloroethane to propan-1-amine

Ans-

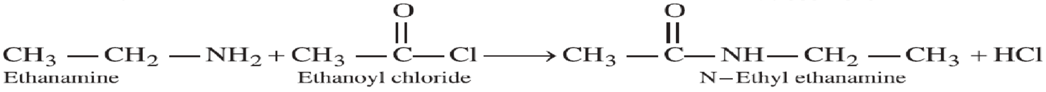
(*i*)



Aniline

Nitrobenzene

(*ii*)



$CH_3-CH_2-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_3 + HCl$

Ethanamine

Ethanoyl chloride

N–Ethyl ethanamine

(*iii*) $\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow{alc.KCN} CH_3-CH_2-CN \xrightarrow[\substack{\text{or}\\ Na/C_2H_5-OH}]{LiAlH_4} \underset{\text{Propan}-1-\text{amine}}{CH_3-CH_2-CH_2-NH_2}$

Q13.

Give one chemical test each to distinguish between the compounds in the following pairs:

(*i*) Methylamine and dimethylamine

(*ii*) Aniline and benzylamine

(*iii*) Ethylamine and aniline

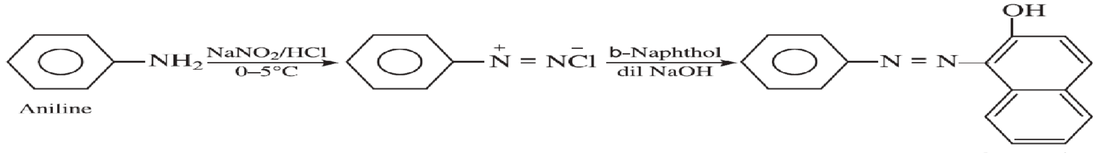
Ans-

(*i*) Methylamine on treatment with alcoholic KOH and $CHCl_3$ gives offensive smell of methyl isocyanide but dimethyl amine does not.

$$\underset{\substack{\text{Methyl amine}\\(1^\circ\text{amine})}}{CH_3-NH_2}+CHCl_3+\underset{(\text{alc})}{3KOH}\longrightarrow \underset{\substack{\text{Ethyl isocyanide}\\(\text{Offensive smell})}}{CH_3-CH_2-NC}+3KCl+3H_2O$$

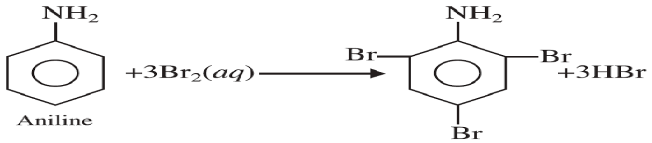
$$\underset{\substack{\text{Dimethyl amine}\\(2^\circ\text{amine})}}{(CH_3)_2NH}\xrightarrow[\Delta]{CHCl_3/KOH}\text{No reaction.}$$

(*ii*) Aniline on treatment with $NaNO_2/HCl$ (HNO2) at 0–5°C followed by treatment with an alkaline solution of β–naphthol gives an orange coloured azodye while benzylamine does not give this test.



Orange dye

(*iii*) Add $Br_2(aq)$, aniline forms white ppt while ethyl amine does not form such ppt.



2, 4, 6–Tribromo aniline
(white ppt)

Q14.

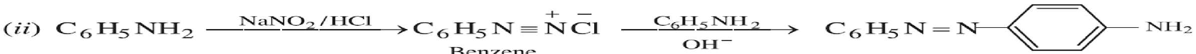
Identify A and B in each of the following processes:

(*i*) $CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{\text{Reduction}} B$

(*ii*) $C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} A \xrightarrow[OH^-]{C_6H_5NH_2} B$

Ans-

(*i*) $CH_3CH_2Cl \xrightarrow{NaCN} \underset{\substack{\text{Ethyl cyanide}\\(A)}}{CH_3CH_2CN} \xrightarrow[Ni/H_2]{\text{reduction}} \underset{\substack{\text{n-Propyl amine}\\(B)}}{CH_3CH_2CH_2NH_2}$



Benzene diazonium chloride (A)

p-Amino-azobenzene (B)

Q15.

In the following cases rearrange the compounds as directed:

(*i*) In an increasing order of basic strength:

$C_6H_5NH_2, C_6H_5N(CH_3)_2, (C_2H_5)_2NH$ and CH_3NH_2

(*ii*) In a decreasing order of basic strength:

Aniline, p-nitroaniline and p-toluidine

(*iii*) In an increasing order of pK_b values:

$C_2H_5NH_2, C_6H_5NHCH_3, (C_2H_5)_2NH$ and $C_6H_5NH_2$

Ans-

(*i*) Increasing order of basic strength is:

$$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$$

(*ii*) *p*-Toluidine > Aniline > tr-nitroaniline

(*iii*) $(C_2H_5)_2\ NH_2 < C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

Q16.

Complete the following chemical equations:

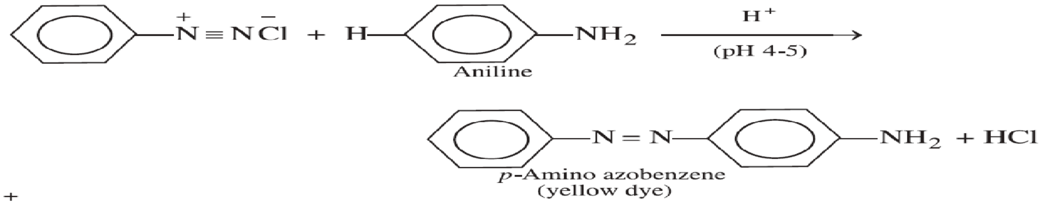
(*i*) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$

(*ii*) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$

(*iii*) $RNH_2 + CHCl_3 + KOH \longrightarrow$

Ans-

(*i*)



(*ii*) $Ar\overset{+}{N_2}\,Cl^- + CH_3-CH_2-OH \longrightarrow ArH + N_2 + CH_3-CHO + HCl$

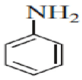
(*iii*) $\underset{1^\circ\ \text{amine}}{R-NH_2} + CHCl_3 + 3KOH(\text{alc.}) \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R-NC} + 3KCl + 3H_2O$

Q17.

Complete the following reactions:

(*i*) $CH_3CH_2NH_2 + CHCl_3 + \text{alc. } KOH \longrightarrow$

(*ii*) $C_6H_5N_2^+Cl^- \xrightarrow[\text{Room temperature}]{H_2O}$

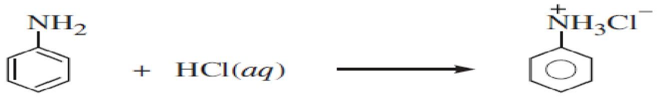
(*iii*) 

$+ HCl(aq) \longrightarrow$

Ans-

(*i*) $CH_3CH_2NH_2 + CHCl_3 + 3KOH(\text{alc.}) \longrightarrow CH_3CH_2NC + 3KCl + 3H_2O$

(*ii*) $C_6H_5N_2^+Cl^- \xrightarrow[\text{Room temperature}]{H_2O} C_6H_5OH + N_2 + HCl$

(*iii*) 

Q18.

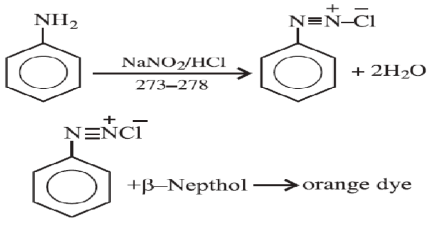
Give the chemical tests to distinguish between the following pairs of compounds:

(*i*) Ethylamine and Aniline

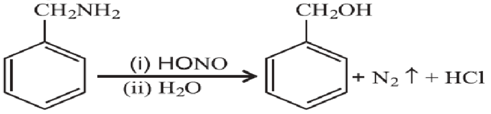
(*ii*) Aniline and Benzylamine

Ans-

(*i*) To distinguish Ethylamine and aniline.

Chemical Test	$C_2H_5NH_2$	$C_6H_5NH_2$
Azo dye Test: Add $NaNO_2$ + dil. HCl at 273 - 278K followed by NaOH and β-naphthol	No reaction	Yellow orange dye is obtained. 

(*ii*) Aniline and Benzyl amine

Chemical Test	Aniline	Benzyl amine
Test: Add nitrous acid ($NaNO_2$/HCl) to both the samples.	No evolution of N_2 gas	N_2 gas is evolved 

Q19.

How will you convert

(*ii*) Ethyl nitrile to ethyl amide

(*iii*) Benzene diazonium chloride to benzonitrile

Ans-

(*ii*) Ethyl nitrile to ethyl amide

$$CH_3—CN \xrightarrow{H_2O/H^+} CH_3—COOH \xrightarrow[\Delta]{NH_3,} CH_3CONH_2$$

(*iii*) Benzene diazonium chloride to benzonitrile

Q20.

Give the chemical tests to distinguish between the following pairs of compounds:

(*i*) Methylamine and Dimethylamine

(*ii*) Aniline and N-methylaniline

Ans-

(*i*) To distinguish CH_3 NH_2 and $CH_3– NH – CH_3$

Reaction with HONO

CH_3NH_2 gives methyl alcohol and N_2 gas.

$$CH_3NH_2 + HONO \xrightarrow{4°C} CH_3OH + N_2 + H_2O$$

Dimethyl amine forms nitroso amine which is water insoluble yellow oil.

$$(CH_3)_2NH + HONO \longrightarrow \underset{\substack{\text{N-Nitroso}\\ \text{dimethyl amine}\\ \text{(yellow oil)}}}{(CH_3)_2N-N=O} + H_2O$$

(*iii*) Aniline and N-methyl aniline

Test: Carbyl amine test:

Aniline on warming with chloroform and **KOH** gives offensive smell of **carbylamine** while N-methyl aniline does not.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\substack{\text{Phenyl}\\ \text{carbylamine}}}{C_6H_5NC} + 3KCl + 3H_2O$$

Q21.

Complete the following reaction equations:

(*i*) $C_6H_5NH_2 + CHCl_3 + KOH \text{ (alc)} \longrightarrow$

(*ii*) $C_6H_5N_2\ Cl + H_3PO_2 + H_2O \longrightarrow$

Ans-

(*i*) $\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH\text{(alco)} \longrightarrow \underset{\text{Phenyl isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$

(*ii*) $\underset{\substack{\text{Benzene diazonium}\\ \text{chloride}}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + HCl + H_3PO_3$

Q22.

Arrange the following compounds in an increasing order of their solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Ans-

Increasing order of solubility of amines in water

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

Q23.

Rearrange the following in an increasing order of their basic strengths:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2$ NH and CH_3NH_2

Ans-

$(C_6H_5)_2 NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$

Q24.

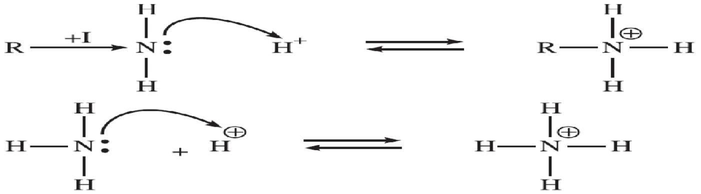
Explain the following giving a reason in each case:

(*i*) Why is an alkylamine more basic than ammonia?

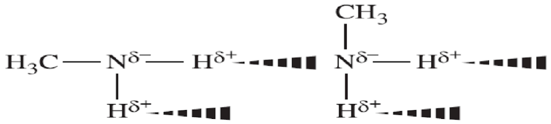
(*ii*) Why do primary amines have higher boiling points than the tertiary amines?

Q25.

(*i*) Alkylamine is more basic than ammonia because in aliphatic amines, the electron releasing alkyl group stabilize their ammonium cations by dispersing the positive charge and in parent amine make the nitrogen unshared electrons more available for sharing with a proton.



(*ii*) The boiling points of primary amine are higher than the tertiary amines because strong intermolecular hydrogen takes place between the molecules of primary amine.



Q26.

Write the structure of N-methylethanamine.

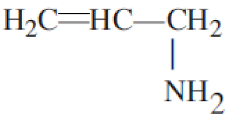
Ans-

CH_3—NH—CH_2CH_3.

Q27.

Write the structure of prop-2-en-1-amine.

Ans-



$H_2C{=}HC{-}CH_2{-}NH_2$

Q28.

(*a*) Explain why an alkylamine is more basic than ammonia.

(*b*) How would you convert

(*i*) Aniline to nitrobenzene

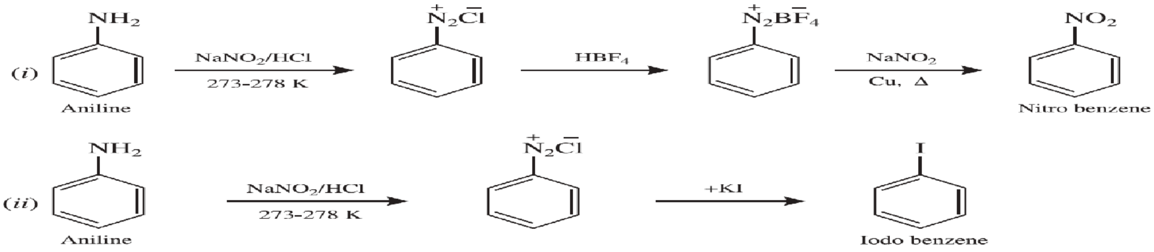
(*ii*) Aniline to iodobenzene?

Ans-

(*a*)

Due to electron releasing nature, the alkyl group (R) pushes electrons towards nitrogen in alkyl amine and thus makes the unshared electron pair more available for sharing with the proton of the acid. Therefore alkyl amine are more basic than ammonia.

(*b*) (*i*)



Q30.

State reasons for the following:

(*i*) pK_b value for aniline is more than that for methylamine.

(*ii*) Ethylamine is soluble in water whereas aniline is not soluble in water.

(*iii*) Primary amines have higher boiling points than tertiary amines.

Ans-

(*i*) In aniline, the lone pair of electrons on N-atom are delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in methylamine, +I-effect of CH_3^- group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than methyamine, hence its pK_b value is more than that for methylamine.

(*ii*) Ethylamine is soluble in water due to formation of inter-molecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic part, *i.e.*, hydrocarbon part, the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.

(*iii*) Due to the presence of two H-atoms on N-atom, primary amines undergo extensive intermolecular hydrogen bonding of a H-atoms on the nitrogen atom, do not undergo H-bonding. As a result, primary amines have higher boiling points than tertiary amines.

Q31.

Give the structures of A, B and C in the following reactions:

(*i*) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(*ii*) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

Ans-

(*i*) $A = C_6H_5CN$, $B = C_6H_5COOH$, $C = C_6H_5CONH_2$

(*ii*) $A = C_6H_5NH_2$, $B = C_6H_5N_2^+Cl^-$, $C = C_6H_5OH$

Q32.

Give the structures of products A, B and C in the following reactions:

(*i*) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(*ii*) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + alc.\ KOH} C$

Ans-

(*i*) $A = CH_3CH_2CN$, $B = CH_3CH_2CH_2NH_2$, $C = CH_3CH_2CH_2OH$

(*ii*) $A = CH_3CONH_2$, $B = CH_3NH_2$, $C = CH_3NC$

Q33.

Illustrate the following reactions giving a chemical equation in each case:

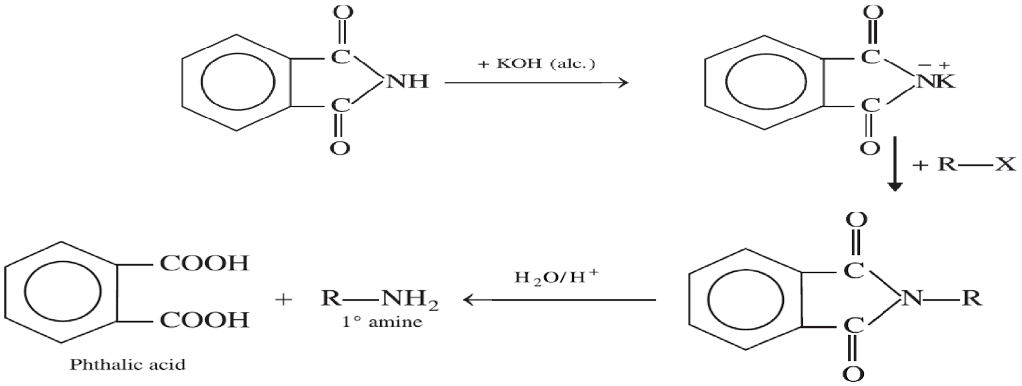
(*i*) Gabriel phthalimide synthesis

(*ii*) A coupling reaction

(*iii*) Hoffmann's bromamide reaction

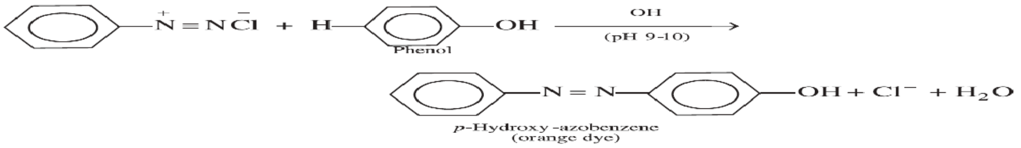
Ans-

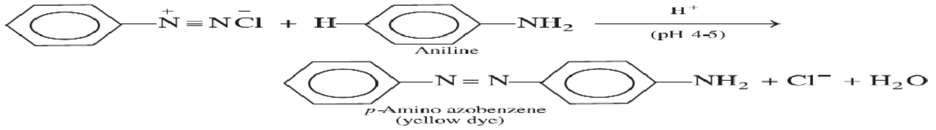
(*i*) **Gabriel phthalimide synthesis:** This reaction is used for the preparation of aliphatic primary amines. In this reaction, phthalimide is first of all treated with ethanolic KOH to form potassium phthalimide. Potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide, which on hydrolysis with dilute hydrochloric acid gives a primary amine as the product.



***(ii)* Coupling reactions:**

Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenol. The mechanism is basically that of electrophilic aromatic substitutions where the diazonium ion is electrophile.

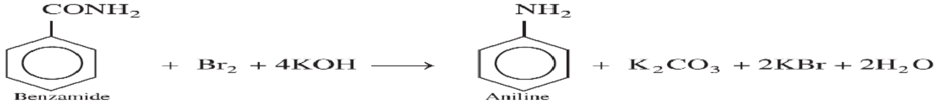




***(iii)* Hoffman's bromamide reaction:**

When a primary acid amide is heated with an aqueous or ethanolic solution of NaOH or KOH and bromine (i.e., NaOBr or KOBr), it gives a primary amine with one carbon atom less.

$$\underset{\text{Acid amide}}{R{-}CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{1^\circ\text{ amine}}{R{-}NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$



Q34.

Arrange the following in decreasing order of their basic strength in aqueous solutions:

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3

Ans-

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

Q35.

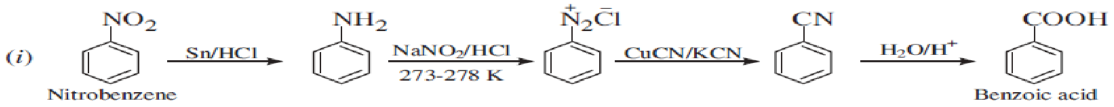
Write chemical equations for the following conversions:

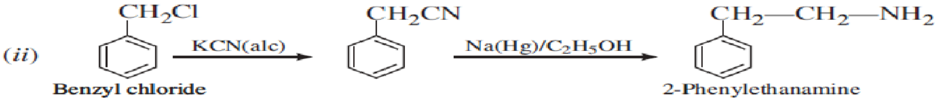
(*i*) Nitrobenzene to benzoic acid

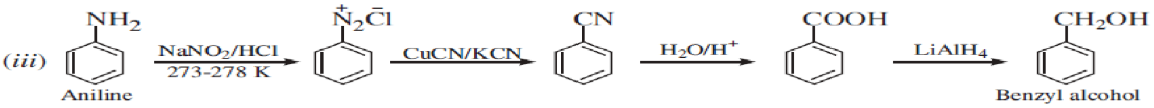
(*ii*) Benzyl chloride to 2-phenylethanamine

(*iii*) Aniline to benzyl alcohol

Ans-







Q35.

Describe the following, giving the relevant chemical equation in each case:

(*i*) Carbylamine reaction

(*ii*) Hoffmann's bromamide reaction

Ans-

(*i*) Carbylamine reaction: Aliphatic and aromatic primary amines when heated with chloroform and ethanolic potassium hydroxide form carbylamines or isocyanides which are foul smelling substances. Secondary and tertiary amines do not show this reaction.

$$R—NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH\ (alc.) \xrightarrow{\Delta} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

(*ii*) Hoffmann's bromamide reaction: When a primary acid amide is heated with bromine in an aqueous or ethanolic solution of NaOH, a primary amine is obtained. The amine so obtained contains one carbon less than that present in the amide.

$$\underset{\text{Acid amide}}{RCONH_2} + Br_2 + 4NaOH \longrightarrow R—NH_2 + Na_2\ CO_3 + 2NaBr + 2H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

Q36.

Complete the following reaction equations:

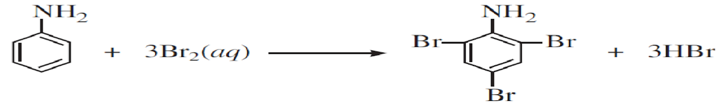
(*i*) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(*ii*) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

Ans-

(*i*) $\underset{\text{Benzene diazonium chloride}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + H_3PO_3 + HCl$

(*ii*)



Aniline

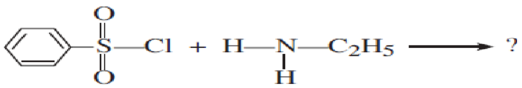
2,4,6-Tribromoaniline

Q37.

Write the main products of the following reactions:

(*i*) $CH_3CH_2NH_2 \xrightarrow[0°C]{HNO_2} ?$

(*ii*)

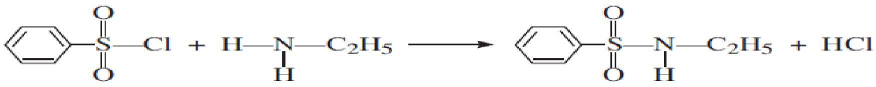


(*iii*)

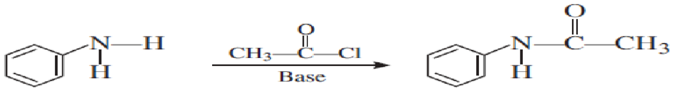
Ans-

(*i*) $CH_3CH_2NH_2 \xrightarrow[0°C]{HNO_2} CH_3CH_2OH$

(*ii*)



(*iii*)



Q38.

How will you convert the following:

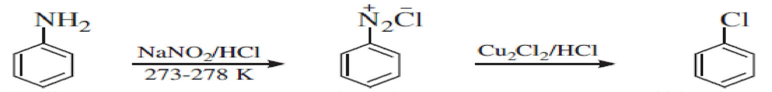
(*i*) Aniline to chlorobenzene

(*ii*) Ethanoic acid to methanamine

(*iii*) Benzene diazonium chloride to phenol

Ans-

(*i*) Aniline to chlorobenzene



Aniline

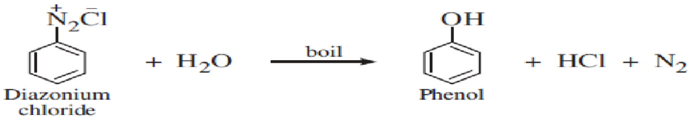
Diazonium salt

Chlorobenzene

(*ii*) Ethanoic acid to methanamine

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2 / KOH} \underset{\text{Methanamine}}{CH_3NH_2}$$

(*iii*) Benzene diazonium chloride to phenol



Q39.

How are the following conversions carried out:

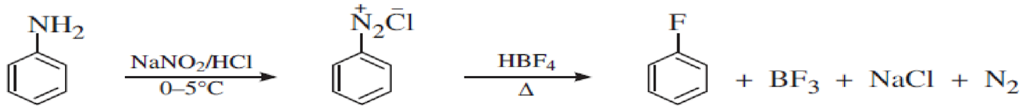
(*i*) Aniline to fluorobenzene

(*ii*) Benzene diazonium chloride to benzene

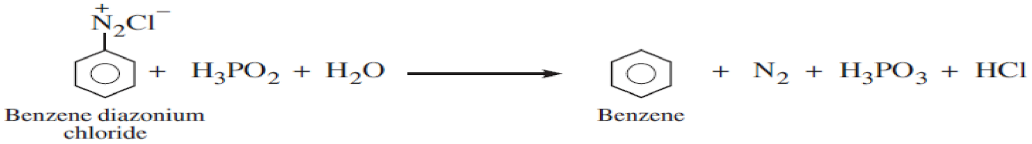
(*iii*) Methyl chloride to ethylamine

Ans-

(*i*) Aniline to fluorobenzene



(*ii*) Benzene diazonium chloride to benzene



(*iii*) Methyl chloride to ethylamine

$$CH_3—Cl \xrightarrow{\text{alc. KCN}} CH_3—CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$

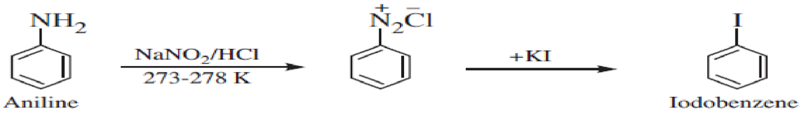
Q40.

How are the following conversions carried out:

(*i*) Aniline to iodobenzene

Ans-

(*i*) Aniline to iodobenzene



BIOMOLECULES

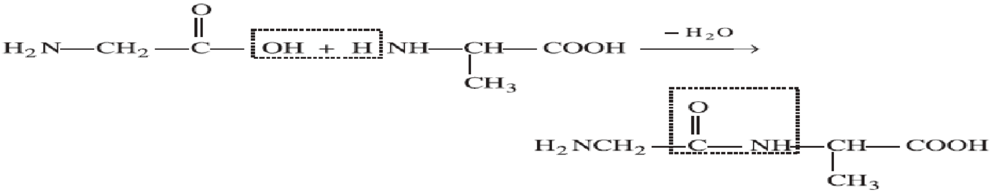
Q.1

Define the following terms in relation to proteins:

(*i*) Peptide linkage (*ii*) Denaturation

Ans-

(*i*) **Peptide linkage:** A peptide linkage is an amide linkage (—CONH—) formed between —COOH group of one α-amino acid and NH_2 group of the other amino acid by the elimination of a water molecule.



Peptide linkage (Gly -Ala)

(*ii*) **Denaturation:** When a protein in its native form is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and proteins loses its biological activity. During denaturation 2° and 3° structures of proteins are destroyed but 1° structure remains intact, *e.g.*, coagulation of egg white on boiling.

Q.2

List the reactions of glucose which cannot be explained by its open chain structure.

Ans-

The following reactions of glucose cannot be explained by its open chain structure.

(*i*) Despite having the aldehyde group glucose does not give 2, 4-DNP test, Schiffs test and it does not form the hydrogen sulphite addition product with $NaHSO_3$.

(*ii*) The pentacetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group.

(*iii*) When D-glucose is treated with methanol in the presence of dry hydrogen chloride gas, it gives two isomeric mono methyl derivatives known as α-D glucoside and methyl β-D glucoside. These glucosides do not react with hydrogen cyanide or with hydroxylamine.

Q3. What are disaccharides? Give an example.

Ans-

Carbohydrates that yield two monosaccharide units, on hydrolysis are called disaccharides, *e.g.,* sucrose.

Q4.

Name the four bases present in DNA. Which one of these is not present in RNA?

Ans-

The four bases present in DNA are adenine (A), guanine (G), cytosine(C) and thymine (T).

Thymine(T) is not present in RNA.

Q5.

What are reducing sugars? Give one example.

Ans-

All carbohydrates which reduce Tollen's reagent and Fehling's solution are referred to as reducing sugars, *e.g.,* glucose.

Define the following in relation to proteins :

(*i*) Primary structure

(*ii*) Denaturation

(*iii*) Peptide linkage

(*i*) **Primary structure of proteins:** The sequence in which various amino acids are arranged in a protein is called its primary structure. Any change in the sequence of amino acids creates different protein which alters biological functions.

(*ii*) **Denaturation:** When a protein in its native form is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and proteins lose its biological activity. During denaturation 2° and 3° structures of proteins are destroyed but 1° structure remains intact, *e.g.,* coagulation of egg white on boiling.

(*iii*) **Peptide linkage:** A peptide linkage is an amide linkage (—CONH—) formed between —COOH group of one α-amino acid and NH_2 group of the other amino acid by the elimination of a water molecule.

Q6.

What happens when D-glucose is treated with the following reagents?

(*i*) HNO_3

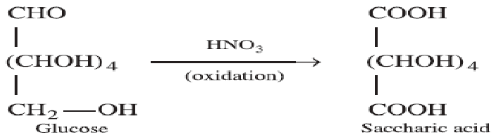
(*ii*) Bromine water

(*iii*) HI

Indicate the products formed.

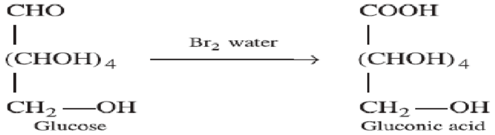
Ans-

(*i*)



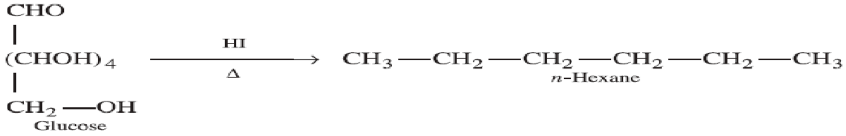
$$\underset{\text{Glucose}}{CHO-(CHOH)_4-CH_2-OH} \xrightarrow[\text{(oxidation)}]{HNO_3} \underset{\text{Saccharic acid}}{COOH-(CHOH)_4-COOH}$$

(*ii*)



$$\underset{\text{Glucose}}{CHO-(CHOH)_4-CH_2-OH} \xrightarrow{Br_2\ \text{water}} \underset{\text{Gluconic acid}}{COOH-(CHOH)_4-CH_2-OH}$$

(*iii*)

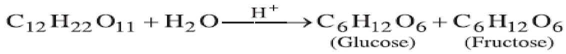


$$\underset{\text{Glucose}}{CHO-(CHOH)_4-CH_2-OH} \xrightarrow[\Delta]{HI} \underset{n\text{-Hexane}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$$

Q7.

Name the products of hydrolysis of sucrose. Why is sucrose not a reducing sugar?

Ans-



$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

Q8.

What are monosaccharides?

Ans-

They are the simplest carbohydrates which do not undergo further hydrolysis, for example: glucose.

Q9.

Explain what is meant by

(*i*) a peptide linkage (*ii*) a glycosidic linkage

(*i*) The $-\overset{\overset{O}{\|}}{C}-NH-$ bond formed between two amino acid molecules with loss of water in a polypeptide is called peptide linkage.

(*ii*) The linkage between two monosaccharides molecules through oxygen atom in a disaccharide or polysaccharide is known as glycosidic linkage.

Ans-

Q10.

Name two water soluble vitamins, their sources and the diseases caused due to their deficiency in diet.

Ans-

B group vitamins and vitamins C are soluble in water.

	Name of Vitamins	**Sources**	**Deficiency diseases**
(*i*)	Vitamin B_{12}	Meat, fish, egg and curd	Pernicious anaemia
(*ii*)	Vitamin C	Citrus fruits and amla	Scurvy

Q11.

Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet.

Ans.

Fat soluble vitamins	**Sources**	**Deficiency diseases**
Vitamin A	Fish liver oil, carrots, milk	Xerophthalmia, Night blindness.
Vitamin D	Exposure to sunlight, fish and egg.	Rickets and osteomalacia.
Vitamin E	Vegetable oils like wheat germ oil, sunflower oil, etc.	Sterility and muscular atrophy
Vitamin K	Green leafy vegetables	Haemorrhages and increased blood clotting time.

Q12.

What are the following substances?

(*i*) Invert sugar (*ii*) Polypeptides

Ans-

(*i*) Invert Sugar: The dextrorotatory sucrose when hydrolysed by boiling with mineral acid produces an equal number of molecules of dextrorotatory fructose. The resulting mixture is laevorotatory and termed as invert sugar.

$$\underset{\substack{\text{Sucrose}\\ [\alpha]_D = 66.5^\circ}}{C_{12}H_{22}OH} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{Glucose}\\ [\alpha]_D = 52.5^\circ}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ [\alpha]_D = -93^\circ}}{C_6H_{12}O_6}}_{\text{Invert sugar}}$$

(*ii*) **Polypeptides:** Polypeptides are polymers formed by condensation of more than ten amino acids. They have large number of peptides bonds in them. Polypeptides are amphoteric because of the presence of terminal-ammonium and carboxylate ions as well as the ionized side chains of amino acid residues

Q13.

What happens when glucose is treated with bromine water?

Ans-

When glucose is treated with bromine water it forms gluconic acid.

$$HOCH_2 - (CHOH)_4 - CHO \xrightarrow{Br_2/H_2O} \underset{\text{Gluconic acid}}{HOCH_2 - (CHOH)_4 - COOH}$$

Q14.

What happens when glucose reacts with nitric acid?

Ans-

Glucose gets oxidised to succinic acid

$$HOCH_2 - (CHOH)_4 - CHO \xrightarrow{HNO_3} \underset{\text{succinic acid}}{HOOC - (CHOH)_4 - COOH}$$

Q15.

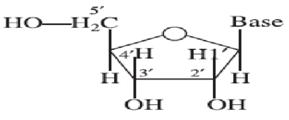
State what the following are and how they differ from each other:

(*i*) a nucleotide, and (*ii*) a nucleoside.

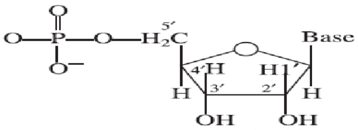
Ans-

(*i*) **Nucleotides:** The monomeric unit of nucleic acid is called nucleotide. When a nucleoside is linked to phosphoric acid at 5' position of sugar moiety, we get nucleotide.

(*ii*) **Nucleoside:** A nucleoside is the condensation product of purine or pyrimidine base with pentose sugar.



Nucleoside



Nucleotide

Q16.

What are essential and non-essential amino acids in human food? Give one example of each type.

Ans-

Essential amino acids: Amino acids which cannot be synthesized in the body but must be obtained through diet, are called essential amino acids. For example: valine, leucine.

Non-essential amino acids: The amino acids, which can be synthesized in the body are known as non-essential amino acids. For example: Glycine, Alanine.

Amino acids may be acidic, alkaline or neutral. How does this happen? What are essential and non-essential amino acids? Name one of each type.

This is due to presence of carboxylic acid as well as amino groups.

- Amino acids which contain two $-\overset{\overset{O}{\|}}{C}-O-H$ group and one $-NH_2$ group are called acidic amino acid, *e.g.*, aspartic acid.
- Amino acids which contain two $-NH_2$ group and one $-\overset{\overset{O}{\|}}{C}-O-H$ group are called basic amino acids, *e.g.*, lysine.
- Amino acids which contain one $-\overset{\overset{O}{\|}}{C}-O-H$ and one $-NH_2$ group are called neutral amino acids, *e.g.*, glycine.
- Amino acids that cannot be synthesized by the body and must be supplied in the diet are called essential amino acids, *e.g.*, lysine, valine, leucine, etc.

The amino acids which are synthesized by our body are called non-essential amino acids, *e.g.*, alanine, glycine, etc.

Q17.

Differentiate between fibrous proteins and globular proteins. What is meant by the denaturation of a protein?

Ans-

Fibrous Proteins	Globular Proteins
1. Consist of linear thread-like molecules which tend to lie side by side to form fibre like structure.	1. Polypeptide chain is folded, around itself forming almost spheroidal shape.
2. Insoluble in water.	2. Soluble in water.
3. Keratin in hair, fibroin in silk, etc.	3. Albumin in eggs, insulin, etc.

Denaturation of Proteins

When a protein in its native form, is subjected to a change in temperature or change in pH, the hydrogen bond are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. During denaturation 2° and 3° structures are destroyed but 1° structures remain intact, *e.g.*, coagulation of egg white on boiling, curdling of milk, etc.

Q18.

Name the bases present in RNA. Which one of these in not present in DNA?

Ans-

The bases present in RNA are adenine (A), guanine (G), cytosine (C) and uracil (U). Uracil is not present in DNA.

Q19.

Explain the meanings of the following terms:

(*i*) Invert sugar (*ii*) Peptide linkage

(*iii*) Denaturation of proteins.

Ans-

(*i*) **Invert Sugar:** The dextrorotatory sucrose when hydrolysed by boiling with mineral acid produces an equal number of molecules of dextrorotatory fructose. The resulting mixture is laevorotatory and termed as invert sugar.

$$\underset{\substack{\text{Sucrose}\\ [\alpha]_D = 66.5^\circ}}{C_{12}H_{22}OH} + H_2O \xrightarrow{H^+} \underbrace{\underset{\substack{\text{Glucose}\\ [\alpha]_D = 52.5^\circ}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ [\alpha]_D = -93^\circ}}{C_6H_{12}O_6}}_{\text{Invert sugar}}$$

(*ii*) **Peptide linkage:** The amide linkage ($-\overset{\overset{O}{\|}}{C}-NH-$) formed between two α–amino acid molecules with the loss of a water molecule in a polypeptide is called a peptide linkage.

(*iii*) **Denaturation of Proteins:** When a protein in its native form, it is subjected to a change, change in temperature or change in pH, the hydrogen bond are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. During denaturation 2° and 3° structures are destroyed but 1° structures remain intact, *e.g.*, coagulation of egg white on boiling, curdling of milk, etc.

Q20.

Describe what you understand by primary structure and secondary structure of proteins.

Ans-

Primary Structure: The specific sequence in which the various α-amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.

Secondary Structure: The conformation which the polypeptide chain assumes as a result of hydrogen bonding is known as secondary structure. The two types of secondary structures are α–helix and β-pleated sheet structure.

In α–helix structure, the polypeptide chain forms all the possible hydrogen bonds by twisting into a right handed screw (helix) with the —NH groups of each amino acid residue hydrogen bonded to the $>C=O$ groups of an adjacent turn of the helix. In β-pleated structure, all peptide chains are stretched out nearly to maximum extension and then laid side by side which are held together by hydrogen bonds.

Q21.

Write the main structural difference between DNA and RNA. Of the four bases, name those which are common to both DNA and RNA.

Ans-

Structural difference between DNA and RNA

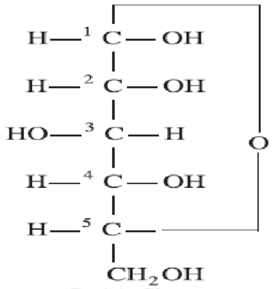
DNA	RNA
1. The sugar present in DNA is 2-deoxy D-(–) ribose.	1. The sugar present in RNA is D-(–)-ribose.
2. DNA has double stranded α-helix structure.	2. RNA has single α-helix structure.

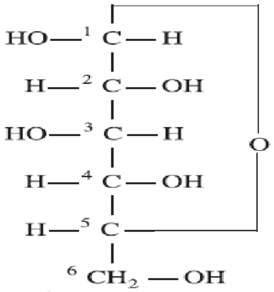
The common bases present in both DNA and RNA are adenine (A), quanine (G) and cytosine (C).

Q22.

What is essentially the difference between α-form of glucose and β-form of glucose? Explain.

Ans-


α−D−(+)−Glucose


β–D–(+)–Glucose

In α-D Glucose, the —OH group at C_1 is toward right whereas in β-glucose, the -OH group at C_1 is towards left. Such a pair of stereo-isomers which differ in the configuration only around C_1 are called anomers.

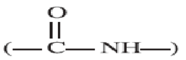
Q23.

Explain what is meant by the following:

(*i*) peptide linkage

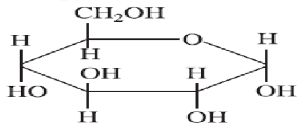
(*ii*) pyranose structure of glucose.

Ans-


$-\overset{\overset{O}{\|}}{C}-NH-$

(*i*) Peptide linkage: The amide ($-\overset{\overset{O}{\|}}{C}-NH-$) linkage between two α-amino acids formed with the loss of a water molecule is called a peptide linkage.

(*ii*) The six membered cyclic structure of glucose is called pyranose structure (α—or β—), in analogy with heterocylic compound pyrane.


α − D − (+) − Glucopyranose

Q24.

Name the products of hydrolysis of (*i*) sucrose and (*ii*) lactose.

Ans-

(*i*) $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or invertase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

(*ii*) $\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or Lactase}]{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$

Q25.

Mention three such facts/reactions about glucose which cannot be explained by its open end structure. What is meant by pyranose structure of glucose?

Ans-

The following facts and reactions cannot be explained by open chain structure of glucose.

(*i*) Despite having the aldehyde group, glucose does give 2, 4-DNP test, Shiff's test and it does not form the hydrogen sulphite addition product with $NaHSO_3$.

(*ii*) The penta-acetate of glucose does not react with hydroxylamine indicating the absence of free aldehydic group.

Q26.

What is meant by (*i*) peptide linkage (*ii*) biocatalysts?

Ans-

(*i*) Peptide linkage is an amide (—$CONH_2$) linkage formed between —COOH group of one α-amino acid and —NH_2 group of other α-amino acid by the loss of a water molecule in a peptide.

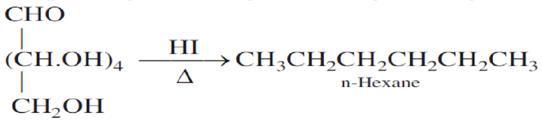
(*ii*) A number of reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are thus termed as biocatalysts. Almost all the enzymes are globular proteins. An enzyme catalyses a biochemical reaction by providing alternate lower activation path thereby increasing the rate of the biochemical reaction. For example, activation energy for acid hydrolysis of sucrose is 6.22 kJ mol^{-1} while the activation energy is only 2.15 kJ mol^{-1} when hydrolyzed in the presence of enzyme sucrose.

Q27.

Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain.

Ans-

On prolonged heating with HI, glucose gives n-hexane.



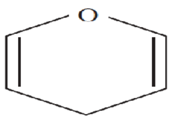
$$\begin{array}{l}\text{CHO}\\ \quad|\\ (\text{CH.OH})_4\\ \quad|\\ \text{CH}_2\text{OH}\end{array} \xrightarrow[\Delta]{\text{HI}} \underset{\text{n-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

Q28.

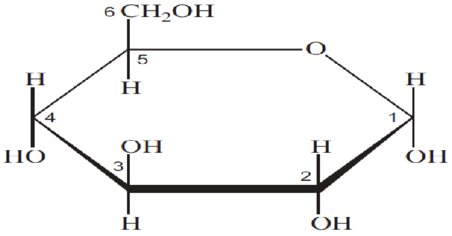
What is essentially the difference between α-glucose and β-glucose? What is meant by pyranose structure of glucose?

Ans-

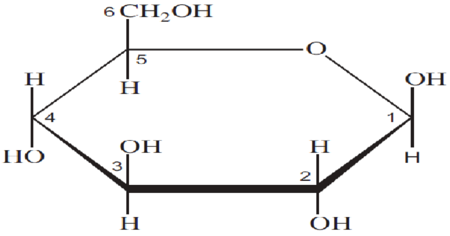
α-Glucose and β-Glucose differ only in the configuration of hydroxy group at C_1 and are called anomers and the C_1 carbon is called anomeric carbon. The six membered cyclic structure of glucose is called pyranose structural (α-or β-), in analogy with pyrane. The cyclic structure of glucose is more correctly represented by Haworth structure as given below.



Pyran



α-D-(+) Glucopyranose



β-D-(+) Glucopyranose