

LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours

ASSIGNMENT PAPER 2

Part A

1. (C) 2. (B) 3. (C) 4. (C) 5. (A) 6. (C) 7. (D) 8. (B) 9. (C) 10. (D) 11. (B) 12. (A) 13. (D) 14. (B)
15. (C) 16. (D) 17. (C) 18. (D) 19. (D) 20. (A) 21. (C) 22. (C) 23. (C) 24. (B) 25. (C) 26. (D) 27. (A)
28. (C) 29. (D) 30. (A) 31. (D) 32. (A) 33. (D) 34. (A) 35. (D) 36. (B) 37. (A) 38. (D) 39. (C) 40. (D)
41. (B) 42. (B) 43. (A) 44. (D) 45. (C) 46. (D) 47. (B) 48. (A) 49. (D) 50. (C)



Part B

Section A

➤ Write the answer of the following questions : (Each carries 2 Mark)

1.



$$\Lambda_m = \frac{\kappa}{c} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 48.15 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{48.15 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1233$$

$$\kappa = \frac{c\alpha^2}{1-\alpha} = \frac{0.001028 \text{ mol L}^{-1} \times (0.1233)^2}{1-0.1233}$$

$$= 1.78 \times 10^{-5} \text{ mol L}^{-1}$$

2.



The order of a reaction is sometimes altered by conditions.



There are many reactions which obey first order rate law although they are higher order reactions.



Consider the hydrolysis of ethyl acetate which is a chemical reaction between ethyl acetate and water. In reality, it is second order reaction and concentration of both ethyl acetate and water affect the rate of the reaction.



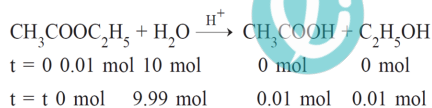
But water is taken in large excess for hydrolysis, therefore, concentration of water is not altered much during the reaction.



Thus, the rate of reaction is affected by concentration of ethyl acetate.

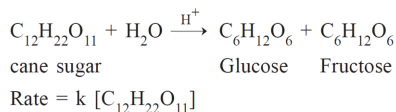


For e.g. 0.01 mol ethyl acetate react with 10 mol of water amounts of the reactants and products at the beginning ($t = 0$) and completion (t) of the reaction are give as under.



The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Inversion of cane sugar is another pseudo first order reaction.



3.



TiCl_3 : The oxidation number of titanium in TiCl_3 is +3. So, the electronic configuration is : $3d^1 3d^1 3d^1$. It has an unpaired electron which makes it paramagnetic, because paramagnetic property is possessed by molecules with unpaired electrons.

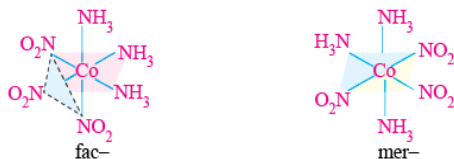
4.



- (i) They have high melting points, which are higher than the melting point of their pure metal
- (ii) They are harder, some boride compounds are diamond-like hardness.
- (iii) They retain metallic conductivity.
- (iv) They are chemically inert

5.

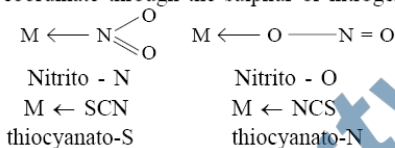
- Another type of geometrical isomerism occurs in octahedral coordination entities of the type $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$.
- If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, it forms the facial (fac) isomer.
- When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



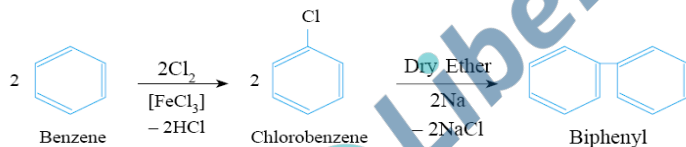
The facial (fac) and meridional (mer) isomers of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

6.

- Ligands that can attach themselves to the central metal atom through two different atoms are called ambidentate ligands.
- Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.
- Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

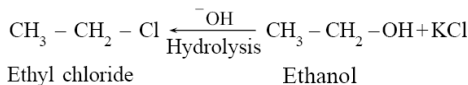


7.



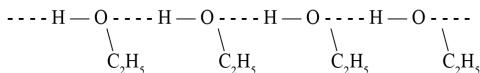
8.

- When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.



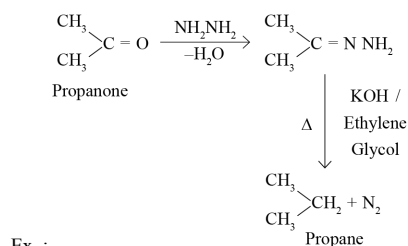
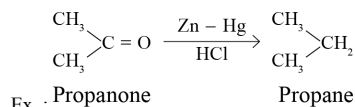
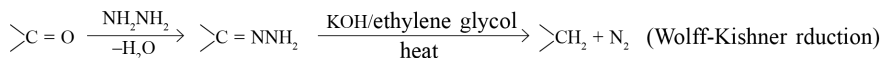
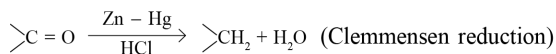
9.

- The molecules of ethanol are associated due to the formation of intermolecular hydrogen bond. Hence, more energy is required to break the inter molecular force of attraction between ethanol molecules, Therefore the boiling point of ethanol is relatively high. Whereas the methoxymethane molecules can readily convert in to vapour because only weak Van der waals force of attraction exist between them. Hence, its boiling point is lower than that of ethanol.



10.

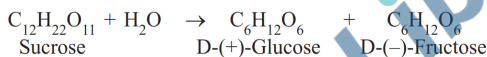
- ➔ Reduction to hydrocarbons: The carbonyl group of aldehydes and ketones is reduced to CH₂ group when treated with zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (Wolff-Kishner reduction).



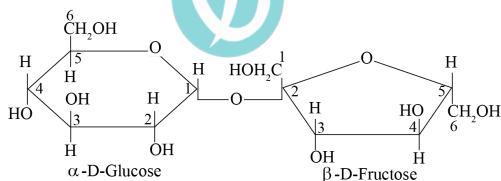
Ex. :

11.

- ➔ One of the common disaccharides is sucrose which on hydrolysis gives equimolar mixture of D-(+)glucose and D-(-)fructose.



- ➔ These two monosaccharides are held together by a glycosidic linkage between C₁ of α-D Glucose and C₂ of β-D fructose.
- ➔ Since the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non reducing sugar.



- ➔ Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose.
- ➔ Since the laevorotation of fructose (-92.4°) is more than dextrorotation of glucose (+52.5°) the mixture is laevorotatory.
- ➔ Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and the product is named as invert sugar.

12.

- ➔ Proteins can be classified into two types on the basis of their molecular shape.

➔ (a) Fibrous protein compounds :

- ➔ When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre-like structure is formed. Such proteins are generally insoluble in water. Some common example are keratin (present in hair, wool, silk) and myosin (present in muscles) etc.

➔ (b) Globular protein compounds :

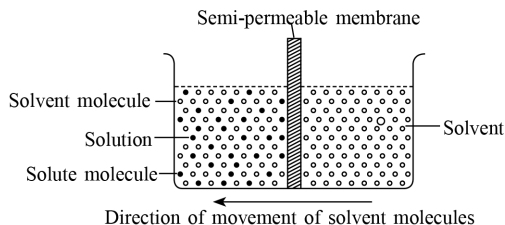
- ➔ This structures results when the chains of polypeptides coil around to give a spherical shape. These are usually soluble in water. Insulin and albumins are the common examples of globular proteins.

Section B

➤ Write the answer of the following questions : (Each carries 3 Mark)

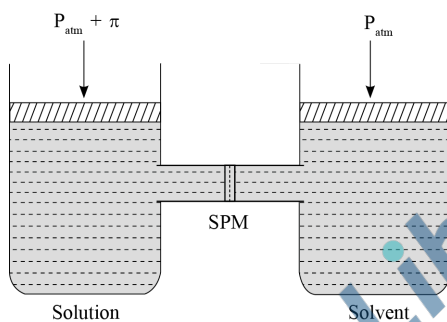
13.

➤ If semi permeable membrane is placed between the solvent and solution as shown fig. the solvent molecules will flow through the membrane from pure solvent to the solution. This process of flow of the solvent is called osmosis.



➤ The flow will continue till the equilibrium is attained

➤ The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. This pressure that just stops the flow of solvent is called osmotic pressure of the solution.



➤ The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis,

➤ Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity.

➤ osmotic pressure is proportional to the molarity, C of the solution at a given temperature T.

$$\pi = CRT$$

Where, π = Osmotic pressure

R = gas constant

$$\therefore \pi = \frac{n_2 RT}{V} \left(\because C = \frac{n_2}{V} \right)$$

$$\pi = \frac{W_2 RT}{M_2 V}$$

W_2 = Wt. of Solute

M_2 = Molar mass of Solute

V = Volume of Solution(L)

T = Temperature

14.

➤ $\text{Mg(s)} \mid \text{Mg}^{2+}(0.001\text{M}) \parallel \text{Cu}^{2+}(0.0001\text{M}) \mid \text{Cu(s)}$

cell reaction : $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$ (n = 2)

$$E^0_{\text{cell}} = E^0_{\text{Cu}^{2+} \mid \text{Cu}} - E^0_{\text{Mg}^{2+} \mid \text{Mg}}$$

$$= 0.34 - (-2.36)$$

$$= 2.70\text{V}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 2.70 - \frac{0.059}{2} \log \frac{0.001}{0.0001}$$

$$= 2.70 - 0.0295$$

$$E_{\text{cell}} = 2.67 \text{ V}$$

15.

➔ "Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants."

➔ Consider the reaction.



➔ Rate of reaction for this reaction can be expressed as

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]^0$$

➔ As any quantity raised to power zero is units.

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k \times 1$$

➔ Thus, the rate of zero order reaction is independent from concentration of reactants.

$$d[\text{R}] = -k dt$$

➔ Integrating both sides

$$[\text{R}] = -kt + I \dots \dots \text{Eq. (1)}$$

Where, I is the constant of integration

➔ At $t = 0$, the concentration of the reactant $\text{R} = [\text{R}]_0$, where $[\text{R}]_0$ is initial concentration of the reactant.

➔ Substituting in equation (1)

$$[\text{R}]_0 = -k \times 0 + I$$

$$[\text{R}]_0 = I$$

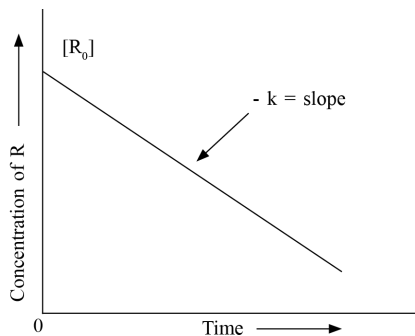
➔ Substituting the value of I in the equation (1)

$$[\text{R}] = -kt + [\text{R}]_0 \dots \dots \text{Eq. (2)}$$

➔ Further simplifying equation (2)

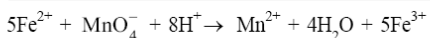
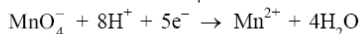
$$k = \frac{[\text{R}]_0 - [\text{R}]}{t} \dots \dots \text{Eq. (3)}$$

➔ Comparing equation (2) with equation of straight line, $y = mx + c$, if we plot $[\text{R}]$ against t , we get a straight line with slope $= -k$ and intercept equal to $[\text{R}]_0$

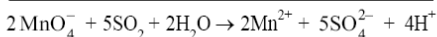
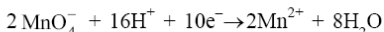


16.

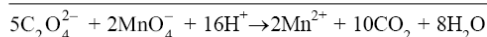
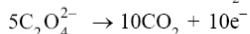
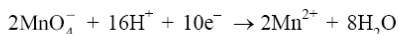
- (i) Acidified KMnO_4 solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.



- (ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid.

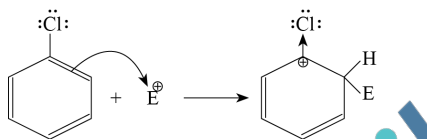


- (iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide.

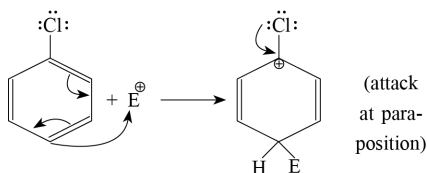
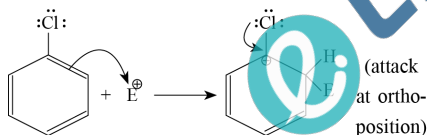


17.

- Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.



Inductive effect destabilises the intermediate carbocation



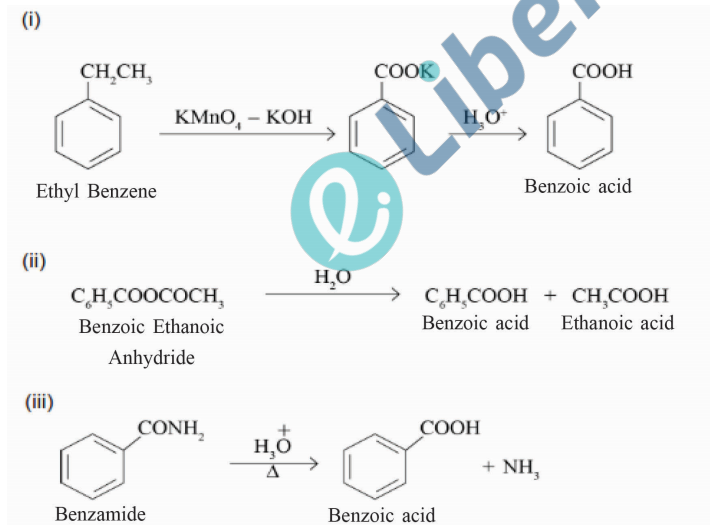
Resonance effect stabilises the intermediate carbocation

- Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at ortho- and para- positions.
- The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation.
- The resonance effect tends to oppose the inductive effect for the attack at ortho- and para- positions and hence, makes the deactivation less for ortho- and para- attack.
- Reactivity is thus, controlled by the stronger inductive effect and orientation is controlled by resonance effect.

18.

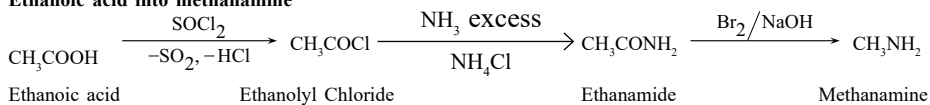
No.	Structure	Type
(i)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$	Primary (1°)
(ii)	$\text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{OH}$	Primary (1°)
(iii)	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	Primary (1°)
(iv)	$\begin{array}{c} \text{OH} \\ \\ \text{CH} - \text{CH}_3 \\ \\ \text{C}_6\text{H}_5 \end{array}$	Secondary (2°)
(v)	$\begin{array}{c} \text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \\ \text{OH} \end{array}$	Secondary (2°)
(vi)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$	Tertiary (3°)

19.



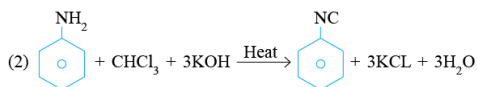
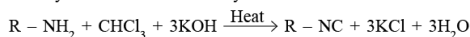
20.

Ethanoic acid into methanamine

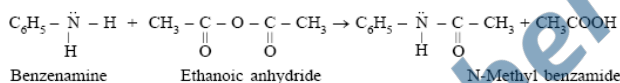
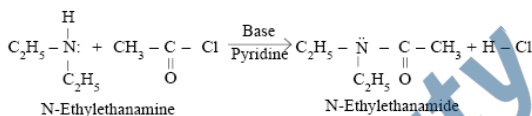
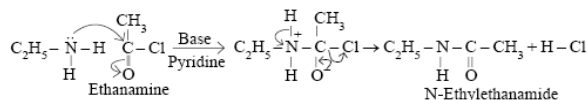


21.

- Aliphatic and aromatic primary amines on heating with chloroform and Ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.
- Secondary and tertiary amines do not show this reaction.
- This reaction is known as carbylamine reaction or isocyanide test and is used as a test for primary amines.



- "Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. This reaction is known as acylation."
- This reaction is the replacement of hydrogen atom of $-NH_2$ and $>N - H$ of group by the acyl group.
- The reaction is carried out in the presence of a base stronger than the amine like pyridine, which removes the formed HCl and shifts the equilibrium to the right hand side.



- Amines also react with benzoyl chloride (C_6H_5COCl) this reaction is known as benzoylation.
- $$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$
- Methanamine Benzoyl chloride N-methylbenzamide

Section C

➤ Write the answer of the following questions : (Each carries 4 Mark)

22.

- Benzene - 1 Benzene - 2
 $p_1^0 = 50.71 \text{ mm Hg}$ $p_2^0 = 32.06 \text{ mm Hg}$
 $W_1 = 80 \text{ g}$ $W_2 = 100 \text{ g}$
 $y_1 = (?)$

- Molar mass of Benzene(C_6H_6)

$$\begin{aligned}
 M_1 &= 6(12) + 6(1) \\
 &= 72 + 6 \\
 &= 78 \text{ g.Mol}^{-1}
 \end{aligned}$$

- Molar mass of toluene($C_6H_5CH_3$)

$$\begin{aligned}
 M_2 &= 7(12) + 8(1) \\
 &= 84 + 8 \\
 &= 92 \text{ g.Mol}^{-1}
 \end{aligned}$$

- Moles of benzene (n_1) = $\frac{1}{M_1} = \frac{80}{78} = 1.02$

- Moles of toluene (n_2) = $\frac{W_2}{M_2} = \frac{100}{92} = 1.087$

- Mole-fraction of benzene (x_1) = $\frac{1.02}{1.02 + 1.087} = 0.484$

➤ Mole-fraction of toluene (x_2) = $1 - 0.484$
= 0.515

➤ According to Raoult's Law

$$\begin{aligned}
 p_{\text{Total}} &= p_1^0 \cdot x_1 + p_2^0 \cdot x_2 \\
 &= (50.71)(0.484) + (32.06)(0.515) \\
 &= 24.54 + 16.51 \\
 &= 41.05 \text{ mm Hg}
 \end{aligned}$$

➤ Mole-fraction of benzene in vapour phase,

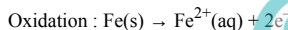
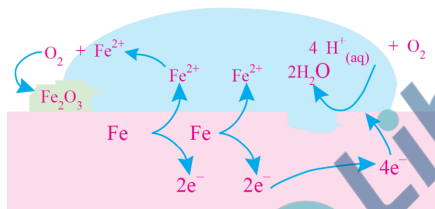
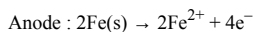
$$\begin{aligned}
 p_1 &= y_1 \cdot p_{\text{Total}} \\
 \therefore p_1^0 \cdot x_1 &= y_1 \cdot p_{\text{Total}} \\
 \therefore \frac{(50.71)(0.484)}{41.05} &= y_1 \\
 \therefore y_1 &= \frac{24.54}{41.05} \quad y_1 = 0.6
 \end{aligned}$$

23.

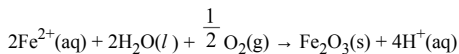
➤ In corrosion, a metal is oxidised by loss of electrons to oxygen and in form of oxides.

➤ Corrosion of iron (commonly known as rusting) occurs in presence of water and air.

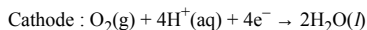
➤ At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction.



Atmospheric oxidation :

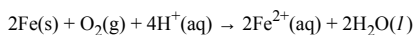


➤ Electrons released at anodic spot move through the metal and go to another spot on the metal, where they reduce oxygen in presence of H⁺ (which is believed to be available from H₂CO₃ formed due to dissolution of carbon dioxide from air into water).



$$E_{\text{H}^+ | \text{O}_2 | \text{H}_2\text{O}}^6 = 1.23 \text{ V}$$

The overall reaction being :



$$E_{\text{(cell)}}^6 = 1.67 \text{ V}$$

➤ The ferrous ions are further oxidised by atmosphere oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide (Fe₂O₃ · x H₂O) and with further production of hydrogen ions.

24.

➤ (A) Calculation of E_a :

➤ For first order reaction, $k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]_t}$

➤ At 298 K temperature, $k_1 = \frac{2.303}{t} \log \frac{100}{90} \dots \dots (I)$

➤ At 308 K temperature, $k_2 = \frac{2.303}{t} \log \frac{100}{75} \dots \dots$ (II)

➤ Dividing Eq. (II) by Eq.(I) we get,

$$\frac{k_2}{k_1} = \frac{\log \frac{100}{75}}{\log \frac{100}{90}} = \frac{0.1249}{0.0458} = 2.73$$

According to Arrhenius equation,

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

$$\log 2.73 = \frac{E_a}{2.303 \times 8.314} \left[\frac{308 - 298}{298 \times 308} \right]$$

$$E_a = \frac{0.4361 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$E_a = 76640 \text{ J/mol} = 76.640 \text{ kJ/mol}$$

(B) Calculation for rate constant k :

➤ According to Arrhenius equation,

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\log k = \log 4 \times 10^{10} - \frac{76640}{2.303 \times 8.314 \times 318}$$

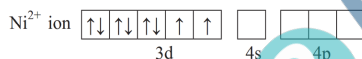
$$\log k = 10.6021 - 12.5870 = -1.9849 = \bar{2}.0151$$

$$k = \text{antilog } \bar{2}.0151$$

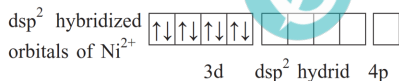
$$k = 1.035 \times 10^{-2} \text{ s}^{-1}$$

25. Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square planar structure is diamagnetic and the $(\text{NiCl}_4)^{2-}$ ion with tetrahedral geometry is paramagnetic.

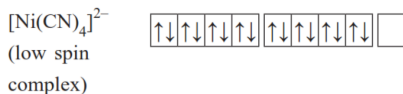
➤ In $[\text{Ni}(\text{CN})_4]^{2-}$ nickel is in +2 oxidation state and has the electronic configuration.



➤ Here, CN^- is strong ligand so electrons of 3d orbital gets paired so hybridization involved is dsp^2



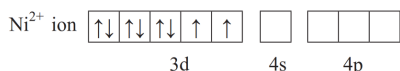
➤ Each of the hybridized orbitals receives a pair of electrons from a cyanide ion.



3d Four pairs of 4p
electrons
from 4 CN^-
groups

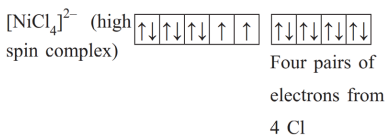
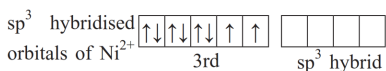
➤ The compound is diamagnetic as evident from the absence of unpaired electron, and square planar complexes.

➤ In $[\text{NiCl}_4]^{2-}$ nickel is in +2 oxidation state and has the electronic configuration



➤ Cl^- is weak ligand so electron does not get paired.

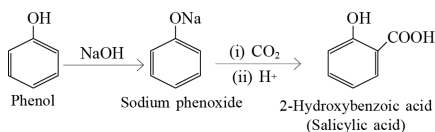
➤ In tetrahedral complexes one s and three p orbitals are hybridized to form four equivalent orbitals oriented tetrahedrally.



➔ Each Cl^- ion donates a pair of electrons. The compound is paramagnetic since, it contains two unpaired electrons, and tetrahedral complex.

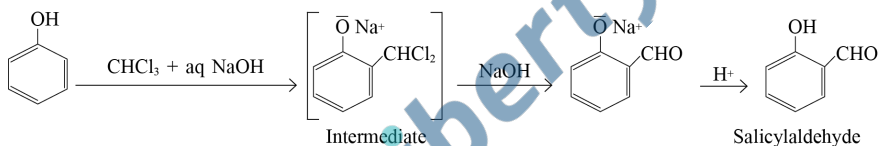
26.

➔ Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Ortho hydroxybenzoic acid is formed as the main reaction product.



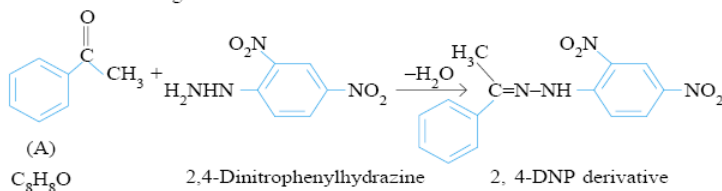
➔ On treating phenol with chloroform in the presence of sodium hydroxide, a $-CHO$ group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction.

➔ The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



27.

(i) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone. (A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Bayer's reagent. This indicates the presence of unsaturation due to an aromatic ring.



(ii)

