LIBERTY PAPER SET

STD. 12 : Chemistry

Full Solution

Time : 3 Hours **ASSIGNMENT PAPER 13**

Part A

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

Part B

Section A

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

1.

- *"Electric conductance through metals is called metallic or electronic conductance and is due to the movement of electrons."*
- The electronic conductance depends on
  - (i) The nature and structure of the metal
  - (ii) The number of valence electrons per atom
  - (iii) Temperature (it decrease with increase of temperature)
- As the electrons enter at one end and exit through the other end, the composition of the metallic conductor remains unchanged of constant.

2.

- Arrhenius equation,
- $k = A\,e^{-\frac{E_a}{RT}}$ ... ... (I)
- $k = 4.5 \times 10^{11}\ s^{-1}\ e^{-\frac{28000\ K}{T}}$ ... ... (II)
- Taking ratio of Eq. (I) and Eq. (II) we get,

$$-\frac{E_a}{RT} = \frac{28000\ K}{T}$$

$$E_a = 28000\ K \times R$$

$$E_a = 28000\ K \times 8.314\ J\ K^{-1}\ mol^{-1}$$

$$E_a = 232792\ J\ mol^{-1} = 232.792\ kJ\ mol^{-1}$$

3.

- *"An alloy is a solid solution of two or more elements in a metallic matrix. It can either be a partial solid solution or a complete solid solution."*
- Alloys are usually found to possess different physical properties than those of the component elements.
- An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94-95%), iron (5%), and traces of S, C, Si, Ca, and Al.
- Uses :
  - Mischmetal is used in cigarettes and gas lighters.
  - It is used in flame throwing tanks.
  - It is used in tracer bullets and shells.

4.

- *"Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds."*
- They are usually non stoichiometric and are neither typically ionic nor covalent,
- For example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc.

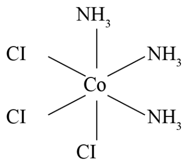
- These compounds are referred to as interstitial compounds.
- The principal physical and chemical characteristics of these compounds are as follows :
    - They have high melting points, higher than those of pure metals.
    - They are very hard, some borides approach diamond in hardness.
    - They retain metallic conductivity.
    - They are chemically inert.

5.

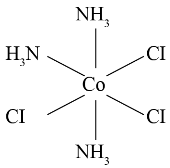
- (i) $[Cr(C_2O_4)_3]^{3-}$

  No geometrical isomers exists for $[Cr(C_2O_4)_3]^{3-}$
- (ii) $[Co(NH_3)_3CI_3]$

  Two geometrical isomers are possible.



Facial



Meridional

6.

- Solution :
    - (i) Hexaamminecobalt(III) Chloride
    - (ii) Potassium hexacyanidoferrate(III)

7.

- In the given molecule, there are four different types of hydrogen atoms. Replacement of these hydrogen atoms will give the following.

  $(CH_3)_2CHCH_2CH_2Cl$,

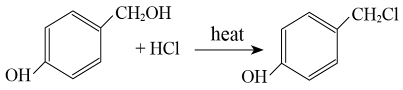
  $(CH_3)_2CHCH(Cl)CH_3$,

  $(CH_3)_2C(Cl)CH_2CH_3$,

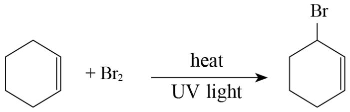
  $CH_3CH(CH_2Cl)CH_2CH_3$

8.

- (i)

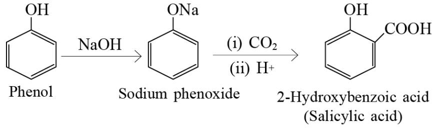


- (ii)



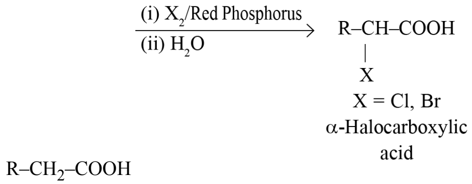
9.

- 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.



10.

- Carboxylic acids having an α-hydrogen are halogenated at the α-position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α-halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.



$$R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2\text{/Red Phosphorus}} \underset{\substack{|\\ X}}{R-CH-COOH}$$

X = Cl, Br
α-Halocarboxylic acid

11.

- Glucose occurs freely in nature as well as in the combined form. It is present in sweet fruits and honey. Ripe grapes also contain glucose in large amounts. It is prepared as follows :
- 1. From sucrose (cane sugar) :
  - If sucrose is boiled with dilute HCl or H_2SO_4 in alcoholic solution, glucose and fructose are obtained in equal amounts.

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

- 2. From starch :
  - Commercial glucose is obtained by hydrolysis of starch by boiling it with dilute H_2SO_4 at 393 K under pressure.

$$\underset{\text{Starch Or cellulose}}{(C_6H_{10}O_5)_n + nH_2O} \xrightarrow[393\,K\ \ 2-3\,atm]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

12.

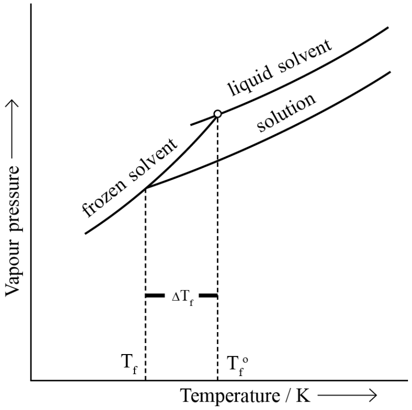
- Carbohydrates are essential for life in both plants and animals.
- They form a major portion of our food.
- Honey has been used for ayurvedic system of medicine.
- Carbohydrates are used as storage molecules as starch in plants and glycogen in animals.
- Cell wall of bacteria and plants is made up of cellulose.
- We build furniture etc. from cellulose in the form of wood and cloth ourselves in the form of cotton fibre.
- They provide raw materials for many important industries like textiles; paper; lacquers and breweries.
- Two aldopentoses viz. D-ribose and 2-deoxy D-ribose are present in nucleic acids.
- Carbohydrates are found in biosystem in combination with many proteins and lipids.

Section B

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

13.

- *Freezing point of a substance may be defined as, “the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase”*
- A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent.
- According to Raoult’s law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature.
- Thus, the freezing point of the solvent decreases.



- Let T_f^0 be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.
- $\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.
- Depression of freezing point (ΔT_f) for dilute solution is directly proportional to molality (*m*) of the solution.

$\Delta T_f \propto m$

$\therefore \Delta T_f = K_f . m$ .....(1)

where, K_f = Molal Depression Constant

OR

Freezing point depression Constant

OR

Cryoscopic constant

- The unit of K_f is k. kg.mol^{-1}

$$m = \frac{W_2 \times 1000}{M_2 \times W_1}$$

- Substituting this value of molality in eq. (1)

$$\Delta T_f = K_f . \frac{W_2 \times 1000}{M_2 \times W_1}$$

$$\therefore M_2 = K_f . \frac{W_2 \times 1000}{\Delta T_f \times W_1}$$

Where, W_2 = wt. of solute

W_1 = wt. of solvent

M_2 = Molar mass of solute

14.

- The cell constant is given by the equation :

cell constant (G*) = conductivity × resistance

$= 1.29 \text{ S/m} \times 100\ \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$

conductivity of 0.02 mol L^{-1} KCl solution = cell constant/resistance

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520\ \Omega} = 0.248 \text{ S m}^{-1}$$

Concentration = 0.02 mol L^{-1}

$= 1000 \times 0.02 \text{ mol m}^{-3}$

$= 20 \text{ mol m}^{-3}$

Molar conductivity $= \wedge_m = \frac{\kappa}{c}$

$$= \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}}$$

$= 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$

Alternatively, $\kappa = \frac{1.29 \text{ cm}^{-1}}{520\ \Omega} = 0.248 \times 10^{-2} \text{ S cm}^{-1}$

and $\wedge_m = \kappa \times 1000 \text{ cm}^3 \text{ L}^{-1} \text{molarity}^{-1}$

$$= \frac{0.248 \times 10^{-2} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.02 \text{ mol L}^{-1}}$$

$= 124 \text{ S cm}^2 \text{ mol}^{-1}$

15.

- For first order reaction,
- $k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{3} = 0.231 \text{ hour}^{-1}$

Calculation for fraction of sample of sucrose remains after 8 hours :

- Taking initial concentration $[R]_0 = 1$ M,
- Concentration after 8 hours $[R]_t = ?$
- $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$

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

$\therefore \log \frac{[R]_0}{[R]_t} = \frac{0.231 \times 8}{2.303}$

$\therefore \log \frac{[R]_0}{[R]_t} = 0.8024$

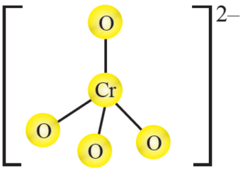
$\therefore \frac{[R]_0}{[R]_t} = \text{anti log } 0.8024 = 6.3445$

$\therefore [R]_t = \frac{[R]_0}{6.3445} = \frac{1}{6.3445} = 0.1576 \text{ M}$

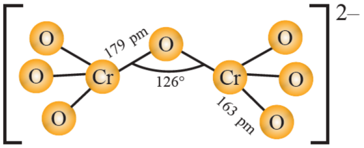
∴ the fraction of sample of sucrose that remains after 8 hours is 0.1576 M.

16.

- The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $Cr_2O_7^{2-}$ are shown below.



Chromate ion

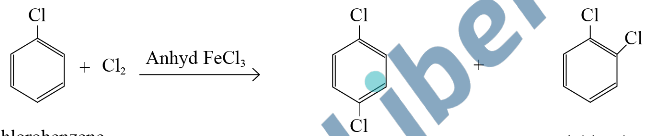


Dichromate ion

- The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126°.
- The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

17.

- (i) Halogenation

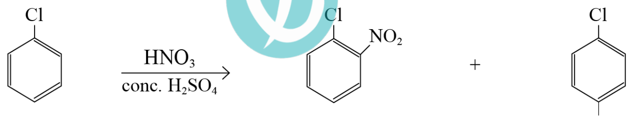


chlorobenzene

1,4-Dichlorobenzene (Major)

1,2-Dichlorobenzene (Minor)

- (ii) Nitration

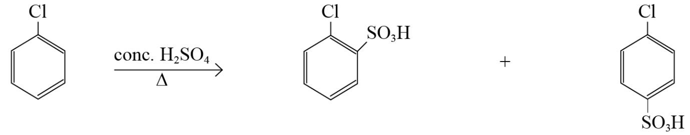


chlorobenzene

1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene (Major)

- (iii) Sulphonation

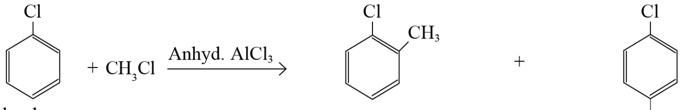


chlorobenzene

2-Chlorobenzenesulphonic acid (Minor)

4-Chlorobenzenesulphonic acid (Major)

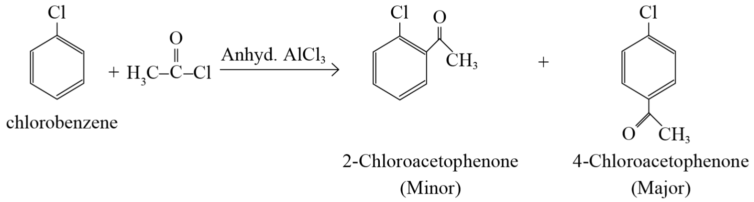
- (iv) Friedel-Crafts reaction



chlorobenzene

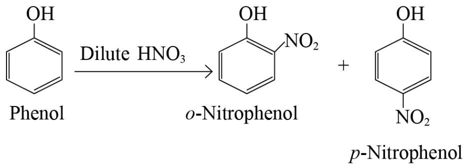
1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)

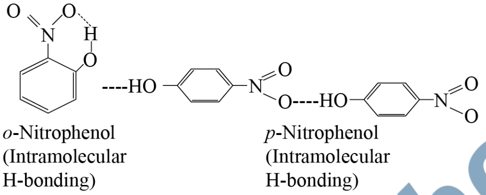


18.

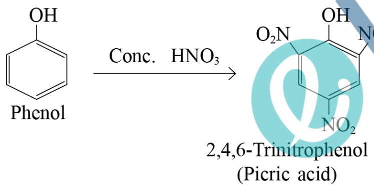
- Nitration: With dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitrophenols.



- The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



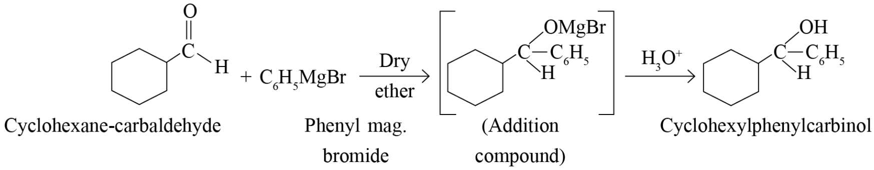
- With concentrated nitric acid, phenol is converted to 2,4,6-trinitrophenol. The product is commonly known as picric acid. The yield of the reaction product is poor.



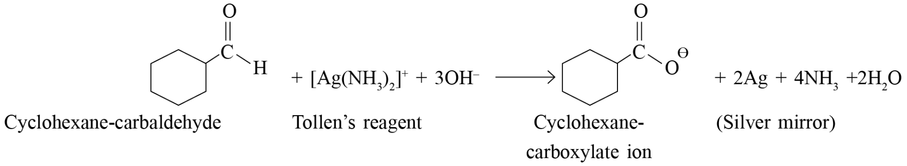
- Nowadays picric acid is prepared by treating phenol first with concentrated sulphuric acid which converts into phenol-2,4-disulphonic acid, and then with concentrated nitric acid to get 2,4,6-trinitrophenol.

19.

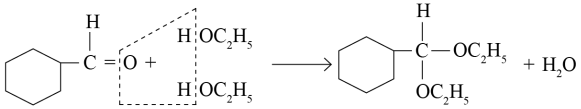
- (i) Reaction of cyclohexanecarbaldehyde with PhMgBr and then H_3O^+ :



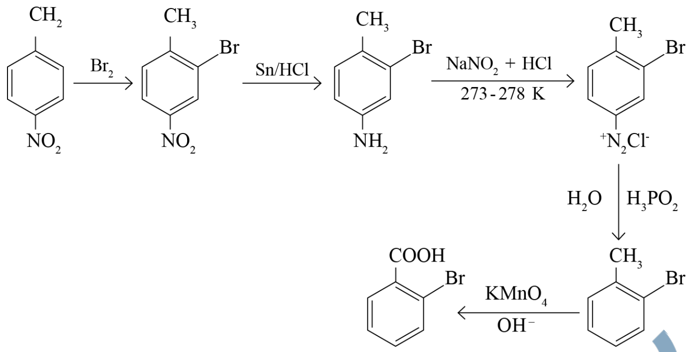
(ii) Reaction of cyclohexane carbaldehyde with Tollen's reagent :



(iii) Reaction of cyclohexane carbaldehyde with excess ethanol and Acid :



20.



21.

(i) CH_3-CH_2-Cl into $CH_3-CH_2-CH_2-NH_2$

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\text{Propanenitrile}}{CH_3-CH_2-C\equiv N} \xrightarrow[H_2/Ni]{\text{Reduction}} \underset{\text{Propane-1-amine}}{CH_3-CH_2-CH_2-NH_2}$$

(ii) $C_6H_5-CH_2-Cl$ into $C_6H_5-CH_2-CH_2-NH_2$

$$\underset{\substack{\text{Chlorophenylmethane}\\\text{(Benzyl Chloride)}}}{C_6H_5-CH_2-Cl} \xrightarrow{\text{Ethanolic NaCN}} \underset{\substack{\text{Phenylethanenitrile}\\\text{(Benzyl cyanide)}}}{C_6H_5-CH_2-C\equiv N} \xrightarrow{H_2/Ni} \underset{\text{2-Phenylethanamine}}{C_6H_5-CH_2-CH_2-NH_2}$$

Section C

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

22.

$W_2 = 30$ g $\qquad W_1 = 90$ g

$M_2 = (?)$ $\qquad p_1 = 2.8$ kPa

$p_1^0 = (?)$

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{\frac{W_2}{M_2}}{\frac{W_2}{M_2} + \frac{W_1}{M_1}}$$

$$\therefore \frac{p_1^0 - 2.8}{p_1^0} = \frac{\frac{30}{M}}{\frac{30}{M} + \frac{90}{18}}$$

$$\therefore 1 - \frac{2.8}{p_1^0} = \frac{\frac{30}{M}}{\frac{30}{M} + 5}$$

$$\therefore 1 - \frac{2.8}{p_1^0} = \frac{\frac{30}{M}}{\frac{30+5M}{M}}$$

$$\therefore 1 - \frac{2.8}{p_1^0} = \frac{30}{5(6+\mathrm{M})}$$

$$\therefore 1 - \frac{2.8}{p_1^0} = \frac{6}{6+\mathrm{M}}$$

$$\therefore 1 - \frac{6}{6+\mathrm{M}} = \frac{2.8}{p_1^0}$$

$$\therefore \frac{6+\mathrm{M}-6}{6+\mathrm{M}} = \frac{2.8}{p_1^0}$$

$$\therefore \frac{\mathrm{M}}{6+\mathrm{M}} = \frac{2.8}{p_1^0} \quad .....(1)$$

➥ after adding 18 g of water

$$\frac{p_1^0 - 2.9}{p_1^0} = \frac{\frac{30}{\mathrm{M}}}{\frac{30}{\mathrm{M}} + \frac{108}{18}}$$

$$\therefore 1 - \frac{2.9}{p_1^0} = \frac{\frac{30}{\mathrm{M}}}{\frac{30}{\mathrm{M}} + 6}$$

$$\therefore 1 - \frac{2.9}{p_1^0} = \frac{\frac{30}{\mathrm{M}}}{\frac{30+6\mathrm{M}}{\mathrm{M}}}$$

$$\therefore 1 - \frac{2.9}{p_1^0} = \frac{30}{6(5+\mathrm{M})}$$

$$\therefore 1 - \frac{2.9}{p_1^0} = \frac{5}{5+\mathrm{M}}$$

$$\therefore 1 - \frac{5}{5+\mathrm{M}} = \frac{2.9}{p_1^0}$$

$$\therefore \frac{5+\mathrm{M}-5}{5+\mathrm{M}} = \frac{2.9}{p_1^0}$$

$$\therefore \frac{\mathrm{M}}{5+\mathrm{M}} = \frac{2.9}{p_1^0} \quad .....(2)$$

➥ Now ratio of eq. (1) & (2)

$$\frac{\frac{\mathrm{M}}{6+\mathrm{M}}}{\frac{\mathrm{M}}{5+\mathrm{M}}} = \frac{\frac{2.8}{p_1^0}}{\frac{2.9}{p_1^0}}$$

$$\therefore \frac{5+\mathrm{M}}{6+\mathrm{M}} = \frac{2.8}{2.9}$$

$\therefore$ (5 + M) 2.9 = (6 + M) 2.8

$\therefore$ 14.5 + 2.9 M = 16.8 + 2.8 M

$\therefore$ 2.9 M – 2.8 M = 2.3

$\therefore$ 0.1 M = 2.3

$\therefore$ M = 23 g/Mol

➥ Substituting value of M in eq. (1)

$$\frac{\mathrm{M}}{6+\mathrm{M}} = \frac{2.8}{p_1^0}$$

$$\therefore \frac{23}{6+23} = \frac{2.8}{p_1^0}$$

$$\therefore p_1^0 = \frac{2.8 \times 29}{23}$$

= 3.53 kPa

23.

- (i) At cathode : The following reduction reactions compete to take place at the cathode.

  $Ag^+(aq) + e^- \rightarrow Ag(s) : E^0 = 0.80\ V$

  $H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g) : E^0 = 0.00\ V$

  The reaction with a higher value of E^0 takes place at the cathode. Therefore deposition of silver will take place at the cathode.

  At Anode : The Ag anode is attacked by NO_3^- ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag^+

- (ii) At cathode : The following reduction reactions compete to take place at the cathode.

  $Ag^+(aq) + e^- \rightarrow Ag(s) : E^0 = 0.80\ V$

  $H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(s) : E^0 = 0.00V$

  The reaction with a higher value of E^0 takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

  At anode : Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2.

  $OH^- \rightarrow OH + e^-$

  $4OH^- \rightarrow 2H\ \ O + O\ \ + 4e^-$

24.

- Reaction $A \rightarrow B$
- Rate = $k[A]^1[B]^0$

  Calculation of rate constant in Experiment-I :

- Rate = k [A]

  $\therefore k = \frac{rate}{[A]} = \frac{2.0 \times 10^{-2}}{[0.1]}$

  $\therefore k = 2.0 \times 10^{-1} = 0.2\ min^{-1}$

  Calculation of [A] in Experiment-II :

  Rate = k [A]

$\therefore [A] = \frac{rate}{k} = \frac{4.0 \times 10^{-2}}{0.2}$

$\therefore [A] = 0.2\ mol\ L^{-1}$

Calculation of initial rate in Experiment-III :

Rate = k [A]

$\therefore rate = 0.2 \times 0.4 = 0.08\ mol\ L^{-1}\ min^{-1}$

Calculation of [A] in Experiment-IV :

Rate = k [A]

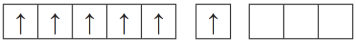
$\therefore [A] = \frac{rate}{k} = \frac{2.0 \times 10^{-2}}{0.2}$

$\therefore [A] = 0.1\ mol\ L^{-1}$

25.

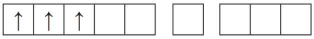
- In $[Cr(NH_3)_6]^{3+}$ oxidation state of Cr is +3.

$_{24}$Cr : [Ar] 3d^5 4s^1 4p



- Electronic configuration of Cr^{3+} ion.

$_{24}Cr^{3+}$: [Ar] 3d^3 4s 4p



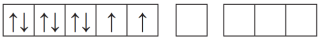
$[Cr(NH_3)_6]^{+3}$: [Ar]

3d^3

d^{2}sp^3 hybrid orbital

- Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals.
- Therefore, it undergoes d^{2}sp^3 hybridization and the electrons in the 3d orbitals remain unpaired. Hence, it is paramagnetic in nature.
- In $[Ni(CN)_4]^{2-}$, Ni exists in the +2 oxidation state. Electronic configuration.

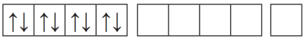
NI^{2+} ion



3d 4s 4p

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

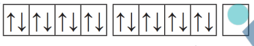
NI^{2+} :



3d dsp^2 hybrid orbital 4p

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

$[Ni(CN)_4]^{-2}$ (low spin complex)



3d Four pair of electrons from 4 CN^- groups

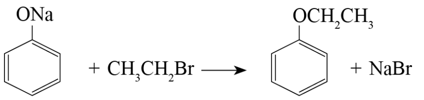
- The compound is diamagnetic as evident from the absence of unpaired electron, and square planar complexes.

26.

- (i) $CH_3CH_2CH_2ONa + CH_3CH_2CH_2Br \longrightarrow C_2H_5CH_2–O–CH_2C_2H_5 + NaBr$

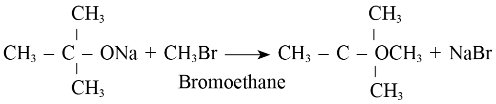
Sodium propoxide 1-Bromopropane 1-Propoxypropane

(ii)



Sodium phenoxide Bromoethane Ethoxybenzene

(iii)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-ONa + CH_3Br \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 + NaBr$$

Bromoethane

Sodium 2 - methyl 2-propoxide 2-Methoxy-2-methylpropane

(iv)

C_2H_5ONa + CH_3Br $\longrightarrow$ $C_2H_5-O-CH_3$ + NaBr

Sodium ethoxide Bromomethane 1-Methoxyethane

27.

- % of carbon = 69.77 %

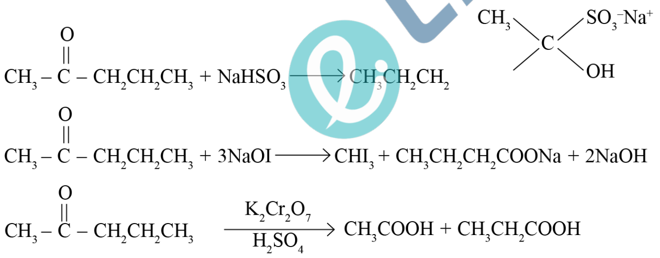
  % of hydrogen = 11.63 %

  % of oxygen = [100 − (69.77 + 11.63)] % = 18.6 %

-

Element	Atomic mass (gm/mol)	Percentage (%)	Atomic ratio = $\frac{\%}{\text{At. mass}}$	Simple ratio	NO. of atoms
C	12	69.77	$\frac{69.77}{12} = 5.81$	$\frac{5.81}{1.16} = 5.0$	5
H	1	11.63	$\frac{11.63}{1} = 11.63$	$\frac{11.63}{1.16} = 10.0$	10
O	16	18.6	$\frac{18.6}{16} = 1.16$	$\frac{1.16}{1.16} = 1.0$	1

- Therefore, the empirical formula of the compound is $C_5H_{10}O$. Now, the empirical formula mass of the compound can be given
- as 5 · 12 + 10 · 1 + 1 · 16
- = 86 gm/mol
- Molecular mass of the compound = 86 gm/mol
- Therefore, the molecular formula of the compound is given by $C_5H_{10}O$.
- Tollen’s reagent is not reduced by the given compound, hence it is not an aldehyde.
- A positive iodoform test is given by the compound and also forms sodium hydrogen sulphate addition products. Since the compound is not an aldehyde, it must be a methyl ketone.
- The given compound also gives a mixture of ethanoic acid and propanoic acid.
- Hence, the given compound is pentan−2−one. $CH_3CH_2CH_2COCH_3$



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2CH_3 + NaHSO_3 \longrightarrow CH_3CH_2CH_2\,C(CH_3)(SO_3^-Na^+)(OH)$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2CH_3 + 3NaOI \longrightarrow CHI_3 + CH_3CH_2CH_2COONa + 2NaOH$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_2CH_2CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + CH_3CH_2COOH$$