

SOLUTIONS

1. (a) Benzaldehyde and benzoic acid can be distinguished by sodium bicarbonate test.

Benzoic acid will give effervescence with NaHCO_3 but benzaldehyde will not react.

(b) Propanal and propanone can be distinguished by their reactions with Tollens' reagent.

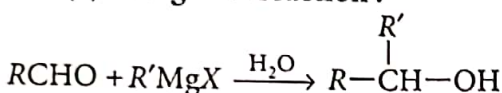
Propanal will form the silver mirror, but propanone does not react.

(c) Benzaldehyde and acetophenone can be distinguished by Tollens' test.

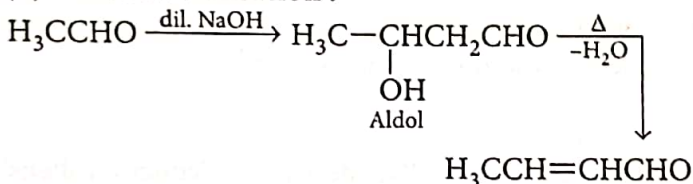
Benzaldehyde will form silver mirror, on treatment with Tollens' reagent whereas acetophenone will not show Tollens' test.

$$\begin{aligned} 2. \text{ Rate} &= -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} \\ &= \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} \end{aligned}$$

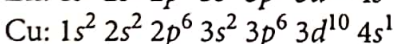
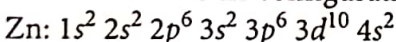
3. (a) Grignard reaction :



(b) Aldol condensation :



4. The electronic configuration of Zn and Cu are:

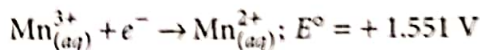
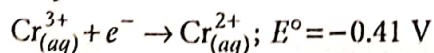


From the above configuration it is clear that first ionisation energy of Zn is greater than that of Cu (because of $4s^2$ and $4s^1$ configuration of Zn and Cu respectively). More energy is needed to remove an electron of $4s^2$ than that of $4s^1$.

The second I.E. of Cu is higher than that of Zn because for Cu^{2+} the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ and for Zn^+ the configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, it is easier to remove $4s^1$ electron of Zn^+ than a $3d$ -electron from $3d^{10}$ (stable configuration).

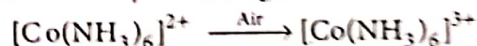
OR

(a) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are



These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

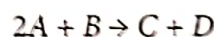
(b) The tendency to form complexes is high for Co(III) as compared to Co(II) . Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, e.g.,



This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7(t_{2g}^6 e_g^1)$ arrangement.

(c) Transition metal ions with d^1 configuration have a tendency to lose this single electron and give ion with a noble gas configuration.

5. For the reaction



The rate law will be; $\text{Rate} = k[\text{A}]^x[\text{B}]^y$

From the given data

$$(r_0)_1 = 6.0 \times 10^{-3} = k_1 (0.1)^x (0.1)^y \quad \dots(1)$$

$$(r_0)_2 = 7.2 \times 10^{-2} = k_2 (0.3)^x (0.2)^y \quad \dots(2)$$

$$(r_0)_3 = 2.88 \times 10^{-1} = k_3 (0.3)^x (0.4)^y \quad \dots(3)$$

$$(r_0)_4 = 2.4 \times 10^{-2} = k_4 (0.4)^x (0.1)^y \quad \dots(4)$$

From equation (1) and (4)

$$\frac{(r_0)_4}{(r_0)_1} = \frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k(0.4)^x (0.1)^y}{k(0.1)^x (0.1)^y}$$

$$4 = \left(\frac{0.4}{0.1}\right)^x = 4^x \quad \therefore x = 1$$

Thus, the order with respect to A is 1.

From equations (2) and (3)

$$\frac{(r_0)_3}{(r_0)_2} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k(0.3)^x (0.4)^y}{k(0.3)^x (0.2)^y}$$

$$4 = \left(\frac{0.4}{0.2}\right)^y \Rightarrow 4 = 2^y \Rightarrow y = 2$$

Thus, the order with respect to B is 2.

The rate law of the reaction is

$$\text{Rate} = k[\text{A}][\text{B}]^2$$

Calculation of rate constant

$$\text{From the rate law, } k = \frac{\text{Rate}}{[\text{A}][\text{B}]^2}$$

From equation (1) (substituting the values of x and y)

$$k_1 = \frac{6.0 \times 10^{-3}}{(0.1)(0.1)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

From equation (2)

$$k_2 = \frac{7.2 \times 10^{-2}}{(0.3)(0.2)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

From equation (3)

$$k_3 = \frac{2.88 \times 10^{-1}}{(0.3)(0.4)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

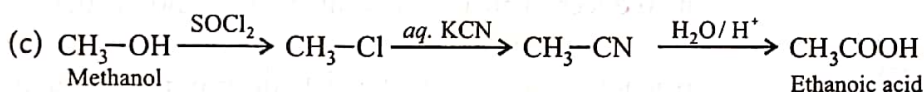
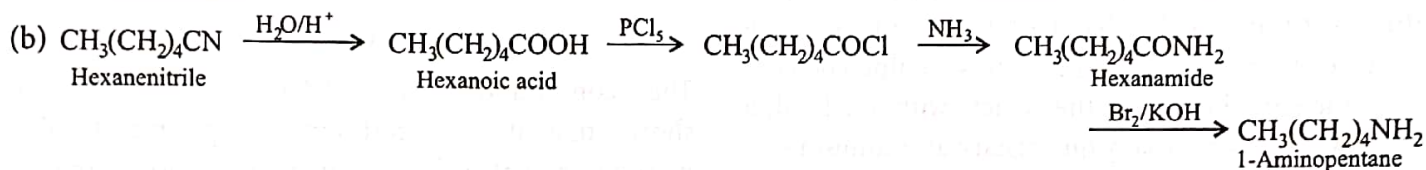
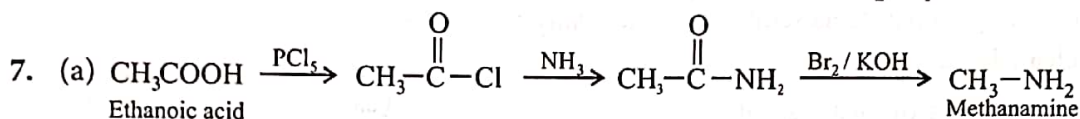
From equation (4)

$$k_4 = \frac{2.4 \times 10^{-2}}{(0.4)(0.1)^2} = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

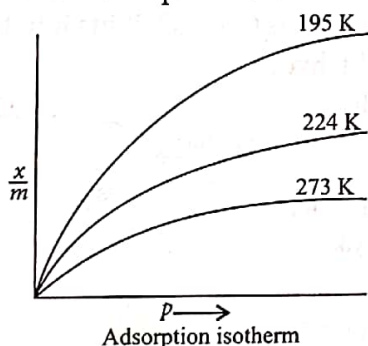
∴ Average $k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

OR

Let us assume the decomposition of N_2O_5 to be a first order reaction, then



8. **Adsorption isotherm** : It is the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.



These curves indicate that on increasing temperature, physical adsorption decreases at a fixed pressure.

Freundlich adsorption isotherm : It is an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$$\frac{x}{m} = kp^{1/n} \quad (n > 1) \quad \dots(i)$$

when, $n = 1, \Rightarrow \frac{x}{m} = kp$

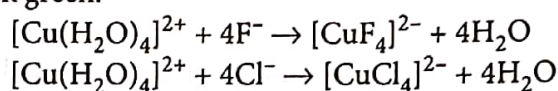
$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad k = \frac{2.303}{t} \log \frac{P_0}{P}$$

$$\text{or } \log P = \frac{-kt}{2.303} + \log P_0$$

Thus a graph of $\log P$ vs t will be linear.

This is in accordance with given statement so the decomposition of N_2O_5 is a first order reaction.

6. An aqueous CuSO_4 solution has $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ as the coordination entity which is of blue colour. The blue colour of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ions changes to green by the addition of F^- or Cl^- ions because both F^- and Cl^- ions are weaker ligands than H_2O . These ions create small splitting (Δ), i.e., low energy light is required for small splitting. Thus light of red colour is absorbed and the $[\text{CuF}_4]^{2-}$ or $[\text{CuCl}_4]^{2-}$ complexes look green.



$$\text{or } \frac{x}{m} \propto p$$

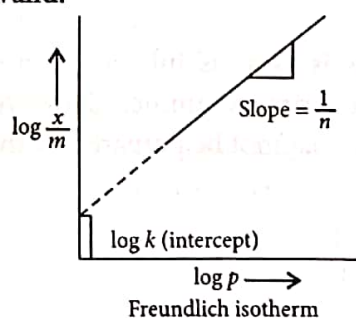
where, x is the mass of gas adsorbed on mass m of the adsorbent at pressure p . k and n are constants which depend on the nature of the adsorbent and the gas at the particular temperature.

Taking log in Eq. (i), gives

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

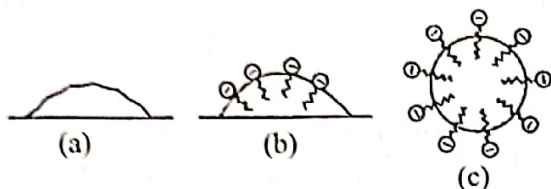
The validity of Freundlich isotherm can be verified by plotting $\frac{x}{m}$ on y -axis and $\log p$ on x -axis.

If it comes to be a straight line, the Freundlich isotherm is valid.

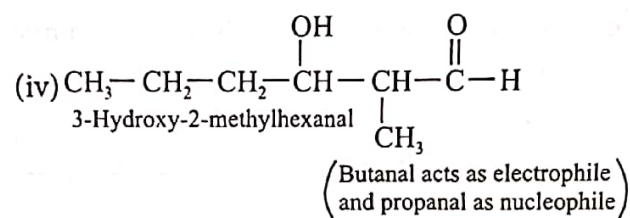
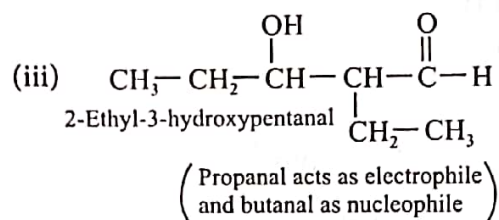
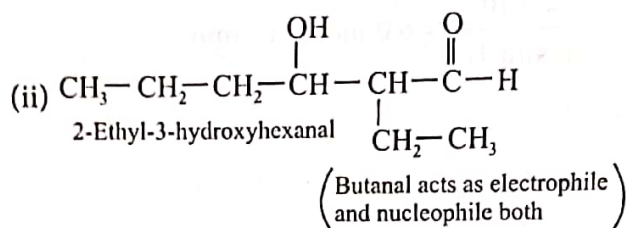
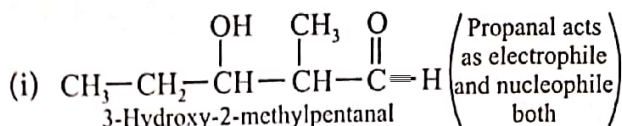


OR

The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part is in the oil droplet and hydrophilic part interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

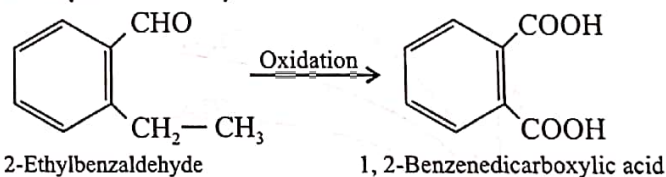


11. The four possible products are :



OR

The compound forms 2,4-DNP derivative. It shows that it is a carbonyl compound. Further it reduces Tollens' reagent which shows that it contains aldehydic group. It undergoes Cannizzaro reaction indicating that aldehyde group is without any α -hydrogen. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid which shows that there are two carbon residues on benzene ring. Since the molecular formula is $\text{C}_9\text{H}_{10}\text{O}$, it fits into the structure, 2-ethylbenzaldehyde.

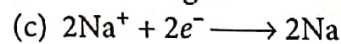


12. (a) $n_{\text{NaCl}} = \frac{4 \times 500}{1000} = 2 \text{ mol}$

(b) n_{Na} deposited = 2 mol

$n_{\text{Na-Hg}}$ formed = 2 mol

Mass of amalgam formed = $2 \times 223 = 446 \text{ g}$



Total charge required = $2F = 2 \times 96500 = 193000 \text{ C}$

(d) 2

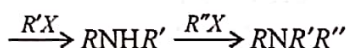
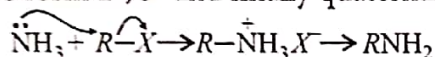
OR

Hydrogen gas

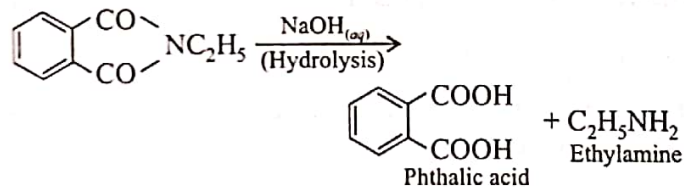
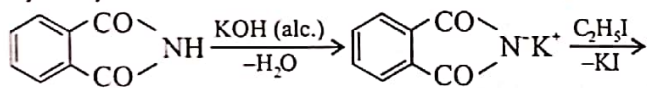


Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium salts when sodium or potassium soaps are dissolved in hard water. These insoluble soaps separate as scum in water and are useless as cleansing agent.

9. (a) **Ammonolysis** : The process of cleavage of the C - X bond in alkyl halides by ammonia molecule is called ammonolysis. 1° amine thus obtained behaves as a nucleophile and further reacts with alkyl halide to form 2° , 3° and finally quaternary ammonium salt.



(b) **Gabriel phthalimide synthesis** : In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an N-alkylphthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.



This synthesis is very useful for the preparation of pure aliphatic primary amines. However, aromatic primary amines cannot be prepared by this method.

