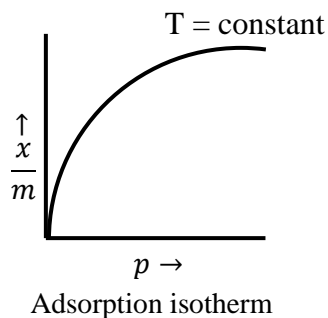


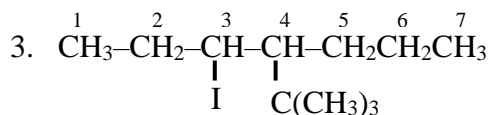
CHEMISTRY

SOLUTION

1. Adsorption isotherm is the variation of the amount of gas adsorbed by the adsorbent with pressure at constant temperature

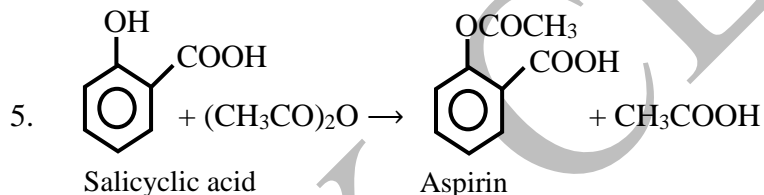


2. The electronic configuration of gadolinium is

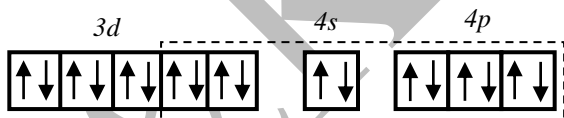


4-tert-butyl-3-iodoheptane

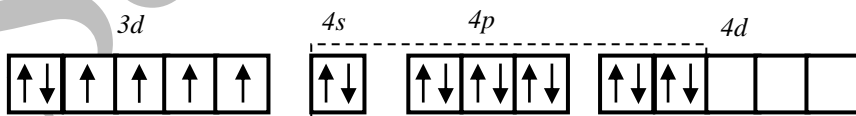
4. Frenkel defect is not found in pure alkali metal halides because alkali metal ions cannot fit into the interstitial sites.



6. In $[\text{Fe}(\text{CN})_6]^{4-}$, CN^- is a strong field ligand hence, pairing of electrons takes place.



In $[\text{Fe}(\text{CN})_6]^{2+}$, H_2O is a weak field ligand hence, pairing does not take place.

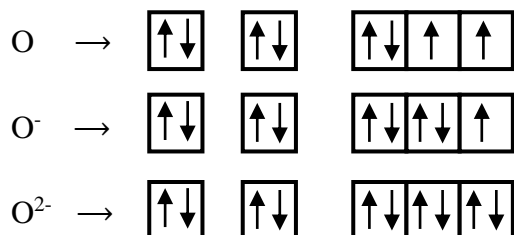


Both ligands show different magnitude of crystal field splitting energy due to different nature hence, absorb different wavelengths and show different colours.

OR

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C π bond is formed by the donation of a pair of electrons from a filled d-orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creastes a synergic effect which strengthens the bond between CO and the metal.

7. This can be explained with the help of electronic configuration.



As O^{2-} has most stable configuration amongst these. So, formation of O^{2-} is much more easier. In solid state, large amount of energy (lattice enthalpy) is released when oxides are formed with divalent O^{2-} ions. It is greater lattice enthalpy of the crystal lattice of oxide (O^{2-}) which compensates for the high energy required to add the second electron.

8. Lowering in freezing point (ΔT_f) = 1.5°C

Mass of solvent (CH_3COOH), $w_1 = 75 \text{ g}$

Mass of solute, $w_2 = ?$

Molar mass of solute, $\text{C}_6\text{H}_8\text{O}_6$, $M_2 = 72 + 8 + 96 = 176 \text{ g mol}^{-1}$

$$\Delta T_f = K_f \times \frac{w_2 \times 1000}{M_2 \times w_1}$$

$$\text{Or } w_2 = \frac{M_2 \times w_1 \times \Delta T_f}{1000 \times K_f} = \frac{176 \times 75 \times 1.5}{1000 \times 3.9} = 5.08 \text{ g}$$

9. We know that for a first order reaction,

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

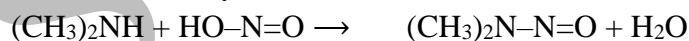
Here, initial concentration, $a = 10 \text{ g}$ and concentration left after time t sec, = 2.5 g , i.e., $(a - x) = 2.5 \text{ g}$

Specific reaction constant, $k = 10^{-3} \text{ sec}^{-1}$

\therefore Time required for the reactant to reduce to 2.5 g

$$= \frac{2.303}{10^{-3} \text{ s}^{-1}} \times \log \frac{10}{2.5} = \frac{2.303}{10^{-3}} \times \log 4 = \frac{2.303}{10^{-3}} \times 0.6021 = 1386.6 \text{ sec}$$

10. These can be distinguished by **Liebermann's** nitrosoamine reaction. $(\text{CH}_3)_2\text{NH}$ (dimethylamine) on treatment with HNO_2 (generated in situ by the action of dil. HCl on NaNO_2) gives yellow coloured oily *N*-nitrosodimethylamine.



N-Nitrosodimethylamine on warming with a crystal of phenol and conc. H_2SO_4 forms a green solution which when made alkaline with aqueous NaOH turns deep blue and then red on dilution.

$(\text{CH}_3)_3\text{N}$ (trimethylamine), on the other hand, being a 3° amines does not give this test.

11. i. Let the number of O^{2-} ions in the crystal be N .

\therefore Number of tetrahedral voids = $2N$

Number of octahedral voids = N

$$\therefore \text{Number of } X^{2+} \text{ ions} = \frac{1}{8} \times 2N = \frac{N}{4}$$

$$\text{Number of } Y^{3+} \text{ ions} = \frac{1}{2} \times N = \frac{N}{2}$$

$$X^{2+} : Y^{3+} : O^{2-} = \frac{1}{4} : \frac{1}{2} : 1 = 1 : 2 : 4$$

\therefore The formula of the compound is XY_2O_4 .

ii. There is one octahedral hole for each atom in hexagonal closed packed arrangement. If the number of oxide ions (O^{2-}) per unit cell is x , then

$$\text{Number of } Fe^{3+} \text{ ions} = \frac{2}{3} \times \text{octahedral holes} = \frac{2}{3} \times x = \frac{2x}{3}$$

$$\therefore \text{Ratio of } Fe^{3+} : O^{2-} = \frac{2x}{3} : x = 2:3$$

Thus, formula of compound is Fe_2O_3 .

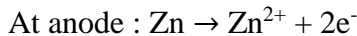
12. i. Zone refining is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

ii. In vapour phase refining, the metal is converted into a suitable volatile compound and then decomposed to give pure metal. So, the two requirements are:

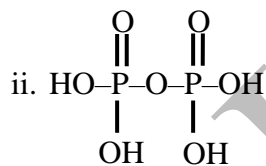
a) The metal should form a volatile compound with a suitable reagent.

b) The volatile compound should be easily decomposable, so that the recovery is easy.

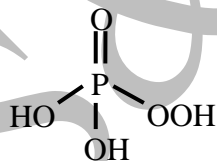
iii. Zinc is refined by electrolytic refining. In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. The more basic metal remains in the solution and the less basic ones go to the anode mud.



13. i. $NO_3^{-} + 3Fe^{2+} + 4H^{+} \rightarrow NO + 3Fe^{3+} + 2H_2O$



Pyrophosphoric acid

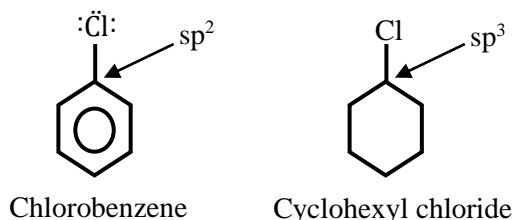


Peroxomonophosphoric acid

14.

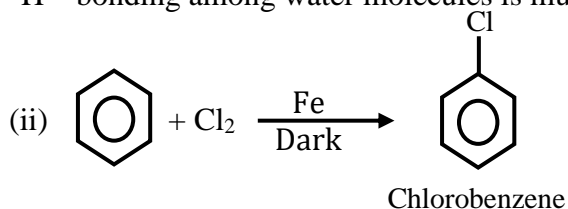
15. (i) (a) There are two reasons :

- i. In case of chlorobenzene, carbon to which chlorine is attached is sp^2 hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised. So, the net dipole moment is lower in chlorobenzene.



- ii. In chlorobenzene C–Cl bond has some double bond character so, its bond length is smaller. Hence, dipole moment is smaller than cyclohexyl chloride which has a longer C–Cl single bond.

(b) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bonding among water molecules is much higher than energy released by water-halide interaction.



16.

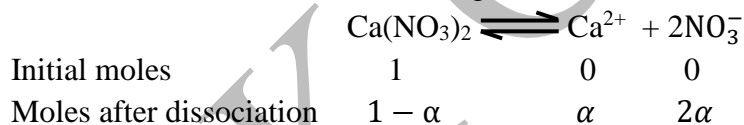
17. Calculated (normal) molecular mass of $\text{Ca}(\text{NO}_3)_2 = 164$.

Calculated (normal) lowering of vapour pressure will be given by

$$\frac{\Delta p}{p^\circ} = \frac{w_2/M_2}{w_1/M_1}$$

$$\therefore \frac{(\Delta p)_{\text{cal}}}{760} = \frac{7/164}{100/18} \text{ or } (\Delta p)_{\text{cal}} = 5.84 \text{ mm}$$

As $\text{Ca}(\text{NO}_3)_2$ is 70% dissociated, degree of dissociation, $\alpha = 0.70$.



$$\text{Total} = 1 + 2\alpha$$

\therefore van't Hoff factor,

$$i = \frac{(\Delta p)_{\text{obs}}}{(\Delta p)_{\text{cal}}} = \frac{1+2\alpha}{1} = 1 + 2\alpha$$

$$\text{or } \frac{(\Delta p)_{\text{obs}}}{5.84} = 1 + 2 \times 0.70$$

$$\text{or } (\Delta p)_{\text{obs}} = 14.0 \text{ mm}$$

$$\text{i.e., } p^\circ - p_s = 14.0 \text{ mm}$$

$$\text{or } p_s = p^\circ - 14.0 = 760 - 14.0 = 746.0 \text{ mm}$$

OR

- i. According to Raoult's law,

$$\text{For toluene, } p_T = p_T^\circ \times x_T$$

$$p_T^\circ = 0.0925 \text{ bar}$$

$$\text{And } x_T = 0.6$$

Then, $p_T = 0.0925 \times 0.6 = 0.0555$ bar

For benzene,

$$p_B = p_B^\circ \times x_B$$

$$x_B = 1 - x_T = 1 - 0.6 = 0.4$$

$$\text{and } p_B^\circ = 0.256 \text{ bar}$$

Then, $p_B = 0.256 \times 0.4 = 0.1024$ bar

Total vapour pressure of solution,

$$P_{\text{total}} = p_T + p_B = 0.0555 + 0.1024 = 0.158 \text{ bar}$$

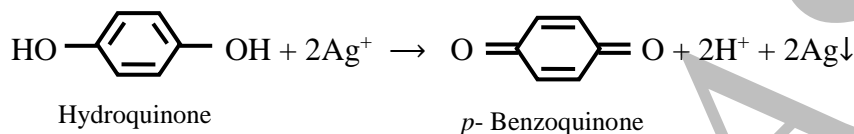
ii. Mole fraction of benzene in vapour phase,

$$y_T = \frac{p_T}{P_{\text{total}}} = \frac{0.0555}{0.158} = 0.351$$

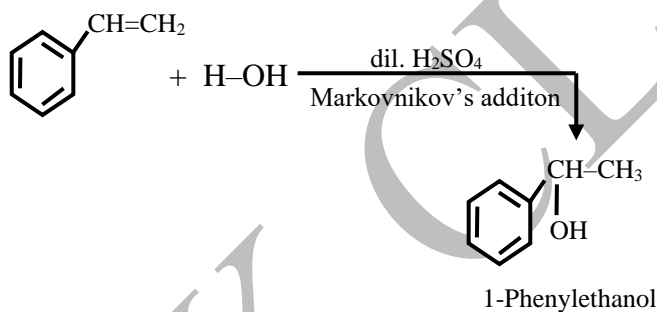
Mole fraction of benzene in vapour phase,

$$y_B = \frac{p_B}{P_{\text{total}}} = \frac{0.1024}{0.158} = 0.648$$

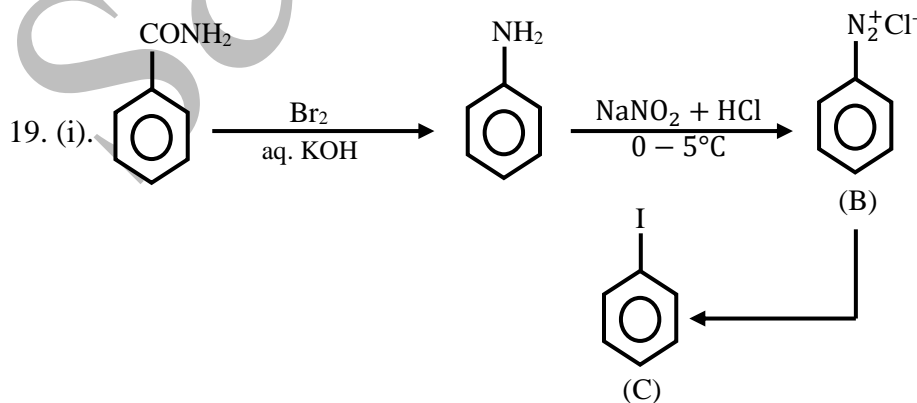
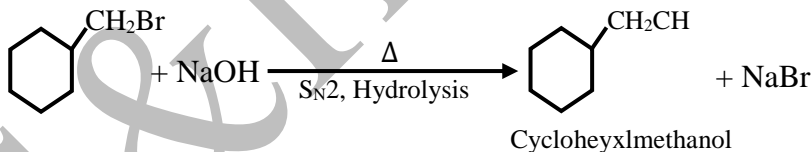
18. (i) Hydroquinone (or benzene- 1,4-diol) is used as a developer in photography because it reduces Ag^+ ions present on the exposed film to metallic silver.



(ii) a. Addition of H_2O to ethenylbenzene (or styrene) in presence of dil. H_2SO_4 gives 1-phenylethanol

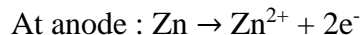


b. Hydrolysis of cyclohexylmethyl bromide by aqueous NaOH gives cyclohexylmethanol.

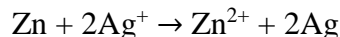


iii. Aspirin acts both as an antipyretic as well as an analgesic. Its analgesic action is due to the reason that it inhibits the synthesis of prostaglandins which stimulate inflammation in the tissues and cause pain.

24. (i) Since, $E_{Ag^+/Ag}^\circ > E_{Zn^{2+}/Zn}^\circ$, the zinc electrode is the anode. The half-cell reactions are as follows:



Overall cell reaction is



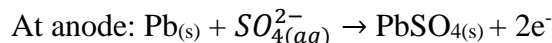
$$\begin{aligned} E_{cell}^\circ &= E_{cathode}^\circ - E_{anode}^\circ = 0.80 \text{ V} - (-0.76) \text{ V} \\ &= 0.80 \text{ V} + (0.76) \text{ V} = 1.56 \text{ V} \end{aligned}$$

Number of electrons involved is 2. Therefore, ΔG° value is given by the formula,

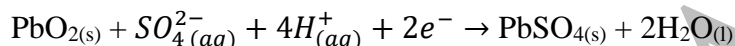
$$\begin{aligned} \Delta G^\circ &= -nFE_{cell}^\circ = -2 \times 96500 \text{ C mol}^{-1} \times 1.56 \text{ V} \\ &= -301080 \text{ J mol}^{-1} = -301.08 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) Lead storage battery is a secondary cell.

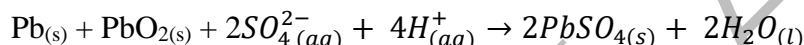
Cell reactions during operation are:



At cathode:

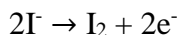
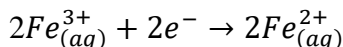


Overall reaction:



OR

(i) Two half reactions for the given redox reactions may be written as:



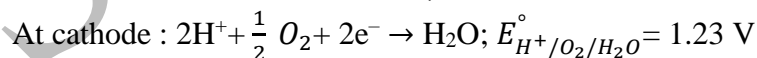
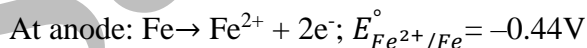
2 moles of electrons are involved in the reaction, so $n = 2$

$$\begin{aligned} \Delta_r G^\circ &= -nFE_{cell}^\circ = -(2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.236 \text{ V}) \\ &= -45548 \text{ J} = -45.55 \text{ kJ} \end{aligned}$$

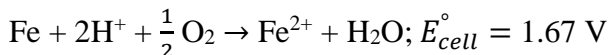
$$\begin{aligned} \log K_c &= -\frac{\Delta G^\circ}{2.303 RT} \\ &= -\frac{(-45.55 \text{ kJ})}{2.303 \times (8.314 \times 10^{-3} \text{ kJ K}^{-1}) \times (298 \text{ K})} = 7.983 \end{aligned}$$

$$K_c = \text{antilog}(7.983) = 9616 \times 10^7$$

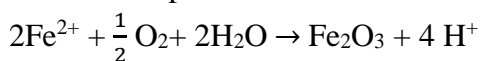
(ii) According to electrochemical theory of rusting, the impure iron surface behaves like small electrochemical cell. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below:

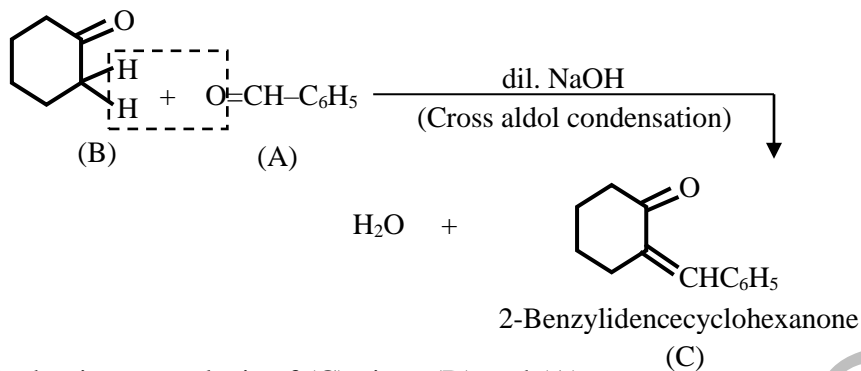


Overall reactions:

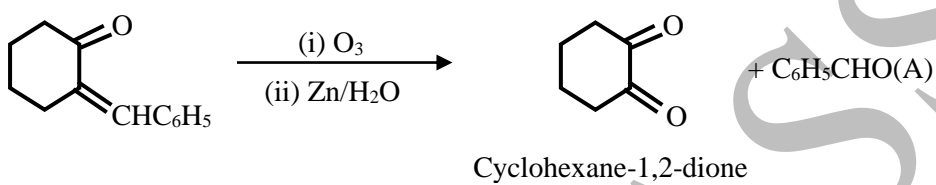


The ferrous ions formed react with the dissolved oxygen or oxygen from the air to form ferric oxide with further production of H^+ ions.





Reductive ozonolysis of (C) gives (D) and (A)



(D) on catalytic reduction gives cyclohexane -1,2-diol (E).

