< SOLUTIONS >

1. (a)
$$\frac{H_3CH_2C}{H_3CH_2C}N-CH_3$$

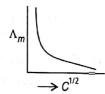
IUPAC name: N-Ethyl-N-methylethanamine

N-Methylpropan-2-amine (2° amine)

(c)
$$H_3C$$
 N-CH₂CH₃

N,N-Dimethylethanamine

2. In weak electrolyte, the conductivity of the solution increases very slowly with dilution of solution and goes on increasing up to infinity. Therefore, it cannot be measured experimentally.



3. (a) *p*-Nitroaniline < Aniline < *p*-Toluidine

$$O_2N$$
— O_2N —

The availability of l.p. on N of p-nitroaniline is drastically reduced by presence of electron withdrawing $-NO_2$ group on it.

In contrast, presence of electron releasing –CH₃ group increases the electron density on N atom and improves basicity in *p*-toluidine.

- (b) $C_6H_5NH_2(I) < C_6H_5NHCH_3(II) < C_6H_5CH_2NH_2(III)$ Involvement of l.p. of N in resonance causes aniline to have low basicity. In II, the –Me group through its +I effect improves the electron density on N and therefore its basic strength increases. In III, the –NH $_2$ is farther off from benzene ring and hence l.p. is localized on it and hence the basic strength is highest.
- 4. In $[Mn(CN)_6]^{3-}$, Mn is in +3 state so, it has configuration of $3d^4$.

Since CN^- is a strong field ligand hence pairing of electrons in 3d-orbital takes place.

Free metal ion
$$1 \cdot \frac{1}{1} \cdot \frac{1}{t_{2g}}$$

In strong octahedral ligand field

So, $[Mn(CN)_6]^{3-}$ has two unpaired electrons. But in $[MnCl_6]^{3-}$, Cl^- is a weak field ligand, so no pairing takes place and it has four unpaired electrons.

OR

The main postulates are:

- (i) In coordination compounds metals show two types of linkages (valencies)-primary and secondary.
- (ii) The primary valencies are normally ionisable and are satisfied by negative ions.
- (iii) The secondary valencies are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.
- (iv) The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.
- 5. Aniline is a weaker base than cyclohexylamine because of resonance.

Resonance structures of aniline are:

$$\overset{:\operatorname{NH}_2}{\longleftrightarrow} \overset{\oplus \operatorname{NH}_2}{\longleftrightarrow} \overset{\oplus \operatorname{NH}_2}{\longleftrightarrow} \overset{\oplus \operatorname{NH}_2}{\longleftrightarrow} \overset{:\operatorname{NH}_2}{\longleftrightarrow} \overset{:\operatorname{NH}_2}{\longleftrightarrow}$$

In case of cyclohexylamine there is no resonance.

6. According to Freundlich adsorption isotherm,

$$\left(\frac{x}{m}\right) = K(p)^{1/n}$$

$$\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log p$$

On comparing this with equation of straight line, we get,

Slope =
$$\frac{1}{2}$$
 = 2
Intercept = log K = 0.4771
 K = antilog (0.4771) = 3

$$\therefore \frac{x}{m} = (3.04)^2 = 3(4 \times 10^{-2})^2 = 48 \times 10^{-4} \text{ g}$$

(a) Physical adsorption of a gas by a solid is generally reversible. Thus,

Solid + Gas ⇌ Gas/Solid + Heat

Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le Chatelier's principle).

- (b) Production of vacuum: Adsorption can be applied to create condition of high vacuum. Vessel which has already been exhausted by vacuum pump is connected to a bulb containing charcoal. The remaining traces of air inspite of low pressure are adsorbed by the charcoal almost completely.
- (c) Solution: In true solution, the size of the particles is about 10^{-10} m.

Colloid: In a colloid, the size of the particles is in between 10^{-7} to 10^{-9} m.

7. (a) Cyanohydrin: Compounds formed when aldehydes or ketones react with hydrogen cyanide are called cyanohydrins.

$$\begin{array}{c}
O \\
\parallel \\
R - C - H + HCN \longrightarrow R - C - CN \\
\text{Aldehyde} & \parallel \\
H \\
Cyanohydrin
\end{array}$$

(b) Acetal: Acetals are the diethers which are formed by the addition of two molecules of alcohols to aldehydes in the presence of dry hydrogen chloride.

$$\begin{array}{c|c}
O & OR' \\
R - C - H + 2R' - OH \xrightarrow{HCl \text{ gas}} R - C - OR' \\
\text{Aldehyde} & H \\
Accetal
\end{array}$$

(c) Semicarbazone : Compounds formed when aldehydes or ketones react with semicarbazide are called semicarbazones.

$$\begin{array}{c|c}
R & & & & & O \\
R' & & & & & & | \\
R' & & & & & & | \\
R' & & & & & & & | \\
R & & & & & & | \\
R' & & & & & & | \\
R' & & & & & & | \\
C = N - NH - C - NH - C$$

OR

O

O

O

I

O

Aq. NaOH

Ethanal

OH

$$CH_3$$
—

 CH_3 —

 CH_3 —

 CH_3 —

 CH_3 —

 CH_3 —

 CH_3 —

OH

 CH_3 —

 CH_3 —

(b)
$$2CH_3 - C - H \xrightarrow{aq. NaOH}$$

$$CH_3 - CH - CH_2 - C - H \xrightarrow{-H_2O}$$

$$CH_3 - CH = CH - C - H$$

$$CH_3 - CH = CH - C - H$$

$$CH_3 - CH = CH - C - H$$

(c)
$$2CH_3 - C - H \xrightarrow{\text{aq. NaOH}}$$

Ethanal

$$CH_3 - CH - CH_2 - C - H \xrightarrow{\Delta}$$

$$CH_3 - CH = CH - C - H \xrightarrow{\text{reagent}}$$

$$CH_3 - CH = CH - C - H \xrightarrow{\text{reagent}}$$

$$CH_3 - CH = CH - C - OH$$

$$CH_3 - CH = CH - C - OH$$

But-2-enoic acid

8. $(A) = [Fe(SCN)(H_2O)_5]^{2+}; (B) = [FeF_6]^{3-}$ IUPAC name of A is : pentaaquathiocyanatoferrate

Spin magnetic moment of (B) =
$$\sqrt{n(n+2)} = \sqrt{5(5+2)}$$

= $\sqrt{5 \times 7}$ or 5.92 BM. [: $n = 5$ in Fe³⁺]

9. Given, Conductivity, $\kappa = 0.0248 \text{ S cm}^{-1}$ Molarity, $C_m = 0.20 \text{ M} = 0.20 \text{ mol L}^{-1}$

Using formula
$$\Lambda_m = \frac{1000 \times \kappa}{C_m}$$

$$\Lambda_m = \frac{(1000 \,\mathrm{cm}^3 \,\mathrm{L}^{-1}) \times (0.0248 \,\mathrm{S \,cm}^{-1})}{(0.20 \,\mathrm{mol} \,\mathrm{L}^{-1})} = 124 \,\mathrm{S \,cm}^2 \,\mathrm{mol}^{-1}$$

Given, $C_m = 0.001 \text{ M}$, $R = 1500 \Omega$, $\kappa = 0.146 \times 10^{-3} \,\mathrm{S \, cm^{-1}}, \,G^* = ?$

Cell constant

=
$$\frac{\text{Conductivity}}{\text{Conductance}}$$
 = $\text{Conductivity} \times \text{Resistance}$
= $(0.146 \times 10^{-3} \text{ S cm}^{-1}) \times (1500 \Omega) = 0.219 \text{ cm}^{-1}$

- 10. (a) A unique feature of lanthanoids is the decrease in atomic and ionic radii from lanthanum to lutetium. The gradual and steady decrease across the period is called lanthanoid contraction.
- (b) (i) Europium (II) has electronic configuration [Xe] $4f^75d^0$ while cerium (II) has electronic configuration [Xe] $4f^{1}5d^{1}$. In Eu²⁺, 4f subshell is halffilled and 5d-subshell is empty. Since half-filled and

completely-filled electronic configurations are more stable, hence Eu²⁺ ions is more stable than Ce²⁺.

- (ii) This is because gadolinium in +3 state has halffilled 4f-subshell $(4f^7)$ and lutetium in +3 state has completely filled 4f-subshell which are very stable configurations.
- 11. (a) Formation of cyanohydrin involves the nucleophilic attack of cyanide ions (CN-) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,2,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.

(b) Although semicarbazide has to -NH2 groups but one of them which is directly attached to carbonyl group, is involved in resonance. So, this nitrogen is not able to act as an effective nucleophile.

$$H_{2}\ddot{\vec{N}} = C - \ddot{N}H - \ddot{N}H_{2} \Longrightarrow H_{2}\dot{\vec{N}} = C - NHNH_{2}$$

So, it is the other — NH, group which acts as nucleophile and is involved in condensation with aldehydes and ketones to give semicarbazone derivatives.

(c) During the preparation of ester from alcohol and carboxylic acid in presence of acid, the water or ester should be removed as fast as it is formed because it is a reversible reaction. If they are not removed, then the reverse reaction also starts and an equilibrium is established, so the overall yield of the ester will be low.

$$\begin{array}{c|c}
O & O \\
\parallel & \parallel \\
R - C - OH + R' - OH \xrightarrow{H_2SO_4} R - C - O - R' + H_2O
\end{array}$$

12. (a) Unit of k for n^{th} order = $(\text{mol L}^{-1})^{1-n} \sec^{-1}...(i)$ Here, $k = 3 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$ Unit of $k = \text{mol}^{-2} L^2 \sec^{-1} \Rightarrow (\text{mol } L^{-1})^{-2} \sec^{-1}$ Comparing (i) and (ii) we get, $1 - n = -2 \Rightarrow n = 3$

(b) Rate
$$= -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$$

(c) Given, $R_1 = k[A]^2 [B]$ According to question, $R_2 = k[3A]^2 [2B]$ $= k \times 9 \ [A]^2 \times 2 \ [B] = 18 \times k \ [A]^2 \ [B] = 18 \ R_1$

(d) Rate $(r) = k[H^+]^n$ When pH = 3; $[H^+] = 10^{-3}$ and when pH = 1; $[H^+] = 10^{-1}$

$$\therefore \quad \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n} \implies \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n \quad (\because r_2 = 100 \, r_1)$$

$$\Rightarrow (10^{-2})^1 = (10^{-2})^n \Rightarrow n = 1$$

Let the order of reaction w.r.t. A is x and w.r.t. B is y.

$$r_1 = k[A]^x [B]^y \qquad \dots (i)$$

$$r_0 = k[2A]^x [B]^y$$
 ...(ii)

$$r_2 = k[2A]^x [B]^y$$
 ...(ii)
 $r_3 = k[A]^x [2B]^y$...(iii)

$$\frac{r_1}{r_2} = \frac{k[A]^x [B]^y}{k[2A]^x [B]^y}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x \Rightarrow x = 2$$

Similarly,
$$\frac{r_1}{r_3} = \frac{k[A]^x [B]^y}{k[A]^x [2B]^y}$$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

Hence the rate law equation is

Rate =
$$k[A]^2[B]^0 \Rightarrow \text{Order of reaction} = 2$$