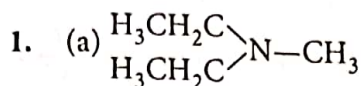
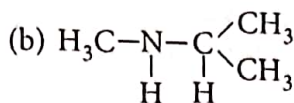


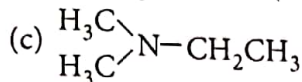
# SOLUTIONS



IUPAC name : *N*-Ethyl-*N*-methylethanamine

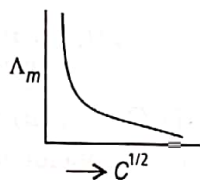


*N*-Methylpropan-2-amine (2° amine)

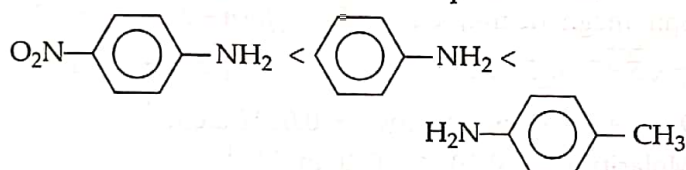


*N,N*-Dimethylethanamine

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



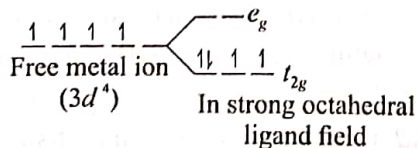
The availability of *l.p.* on N of *p*-nitroaniline is drastically reduced by presence of electron withdrawing  $-\text{NO}_2$  group on it.

In contrast, presence of electron releasing  $-\text{CH}_3$  group increases the electron density on N atom and improves basicity in *p*-toluidine.

(b)  $\text{C}_6\text{H}_5\text{NH}_2$ (I) <  $\text{C}_6\text{H}_5\text{NHCH}_3$ (II) <  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (III)  
Involvement of *l.p.* of N in resonance causes aniline to have low basicity. In II, the  $-\text{Me}$  group through its +I effect improves the electron density on N and therefore its basic strength increases. In III, the  $-\text{NH}_2$  is farther off from benzene ring and hence *l.p.* is localized on it and hence the basic strength is highest.

4. In  $[\text{Mn}(\text{CN})_6]^{3-}$ , Mn is in +3 state so, it has configuration of  $3d^4$ .

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



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

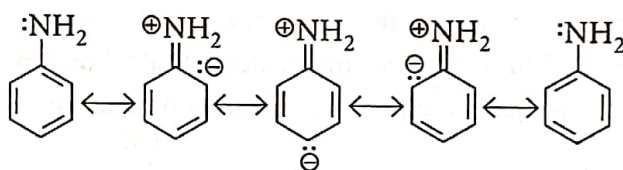
OR

The main postulates are :

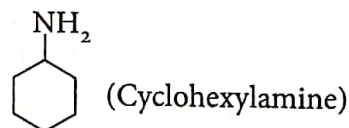
- In coordination compounds metals show two types of linkages (valencies)-primary and secondary.
- The primary valencies are normally ionisable and are satisfied by negative ions.
- The secondary valencies are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.
- 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 :



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,

$$\text{Slope} = \frac{1}{n} = 2$$

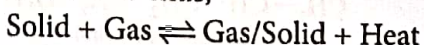
$$\text{Intercept} = \log K = 0.4771$$

$$K = \text{antilog}(0.4771) = 3$$

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

OR

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

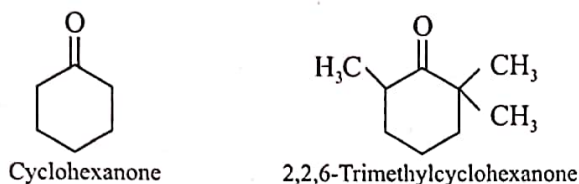




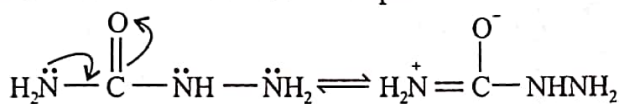
completely-filled electronic configurations are more stable, hence  $\text{Eu}^{2+}$  ions is more stable than  $\text{Ce}^{2+}$ .

(ii) This is because gadolinium in +3 state has half-filled 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 ( $\text{CN}^-$ ) at the carbonyl carbon. In cyclohexanone, reaction proceeds but in 2,2,6-trimethylcyclohexanone, the methyl groups cause steric hindrance and yields are poor.

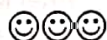
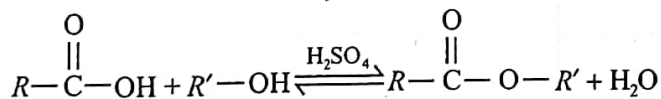


(b) Although semicarbazide has two  $-\text{NH}_2$  groups but one of them which is directly attached to carbonyl group, is involved in resonance. So, this nitrogen is not able to act as an effective nucleophile.



So, it is the other  $-\text{NH}_2$  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.



12. (a) Unit of  $k$  for  $n^{\text{th}}$  order =  $(\text{mol L}^{-1})^{1-n} \text{sec}^{-1}$  ... (i)

Here,  $k = 3 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$

Unit of  $k = \text{mol}^{-2} \text{ L}^2 \text{ sec}^{-1} \Rightarrow (\text{mol L}^{-1})^{-2} \text{sec}^{-1}$  ... (ii)

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 ( $r$ ) =  $k[\text{H}^+]^n$

When  $\text{pH} = 3$ ;  $[\text{H}^+] = 10^{-3}$

and when  $\text{pH} = 1$ ;  $[\text{H}^+] = 10^{-1}$

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

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

OR

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

$$r_1 = k[A]^x [B]^y \quad \dots \text{(i)}$$

$$r_2 = k[2A]^x [B]^y \quad \dots \text{(ii)}$$

$$r_3 = k[A]^x [2B]^y \quad \dots \text{(iii)}$$

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

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

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

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

Hence the rate law equation is

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