

# QUESTIONS FOR PRACTICE SOLUTIONS

## CHAPTER-1 Electrochemistry

### 1. (i) Variation of Molar Conductivity $\Lambda_m$ with concentration for weak electrolytes

A weak electrolyte does not ionise much in solution. Due to low concentration of free ions in solution at moderate concentrations, the molar conductivity of the solution of a weak electrolyte is quite low, much lower than that of a strong electrolyte. As the concentration of the solution is decreased there is a steep rise in the molar conductivity of weak electrolyte due to increase in ionisation.

### (ii) Variation of Molar Conductivity $\Lambda_m$ with concentration for strong electrolytes

A strong electrolyte is almost completely ionised at all dilutions. Therefore, an increase in dilution does not appreciably increase the number of ions in the solution of a strong electrolyte. The slight change in the molar conductivity of strong electrolytes with change in concentration is actually due to a change in the interionic attractions. This can be explained as follows.

When the concentration of the solution of a strong electrolyte is increased (i.e., dilution is decreased), the number of ions per unit volume decreases. Thus, the oppositely charged ions come closer and experience a greater interionic attraction. This results in a decrease in the molar conductivity of the solution.

### 2. Conductivity of acetic acid solution is

$$\kappa = \frac{K}{R} = \frac{2.0 \text{ cm}^{-1}}{3765 \Omega} = 5.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1} \quad \therefore R = \rho \frac{l}{A}, \kappa = \frac{1}{\rho}$$

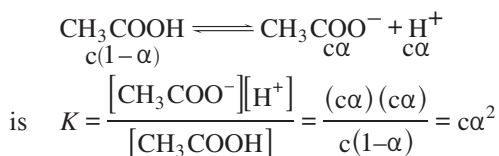
Molar conductivity of 0.1 M acetic acid solution is  $\therefore R = \frac{1}{\kappa} \frac{l}{A}$  and  $\frac{l}{A} = K$  (cell constant)

$$\Lambda_m = \frac{K}{C} = \frac{5.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}}{0.1 \text{ mol dm}^{-3}} = 5.3 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1} \text{ dm}^3 \text{ mol}^{-1} = 5.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Degree of dissociation of 0.1 M acetic acid is

$$\alpha = \frac{\Lambda_m}{\lambda_m^\infty(\text{H}^+) + \lambda_m^\infty(\text{Ac}^-)} = \frac{5.3}{(349.8 + 40.9)} = 0.0136$$

The equilibrium constant of



Substituting the values, we get

$$K = (0.1 \text{ M})(0.0136)^2 = 1.84 \times 10^{-5} \text{ M}$$

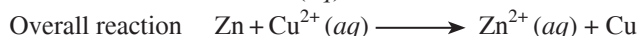
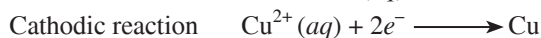
### 3. The formula of potash alum is $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Thus, at infinite dilution of 1 mol of potash alum will produce 2 mol of $\text{K}^+$ , 2 mol of $\text{Al}^{3+}$ and 4 mol of $\text{SO}_4^{2-}$ . Hence

$$\begin{aligned} \Lambda_m^\infty(\text{potash alum}) &= 2 \Lambda_m^\infty(\text{K}^+) + 2 \Lambda_m^\infty(\text{Al}^{3+}) + 4 \Lambda_m^\infty(\text{SO}_4^{2-}) \\ &= (2 \times 73.5 + 2 \times 189 + 4 \times 160) \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} = 1165 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

Since total positive (or negative) charge carried by 1 molecule of potash alum is 8, we will have

$$\Lambda_{eq}^\infty(\text{potash alum}) = \left( \frac{\Lambda_{eq}^\infty \text{ potash alum}}{8 \text{ eq mol}^{-1}} \right) = \frac{1165 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}{8 \text{ eq mol}^{-1}} = 145.6 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

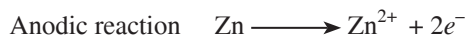
4. We have,



$$\text{EMF of the cell} \quad E_{\text{cell}}^{\circ} = E_{\text{R}}^{\circ} - E_{\text{L}}^{\circ} = 0.350 \text{ V} - (-0.763 \text{ V}) = 1.113 \text{ V}$$

Since  $E_{\text{cell}}^{\circ}$  is positive, the cell reaction is spontaneous.

5. The half-cell reactions are



The Nernst equation for the cell reaction is

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]p(\text{H}_2)}{[\text{H}^{+}]^2}$$

$$\text{Where} \quad E^{\circ} = E_{\text{H}^{+}|\text{H}_2|\text{Pt}}^{\circ} - E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} = 0 - (-0.763 \text{ V}) = 0.763 \text{ V}$$

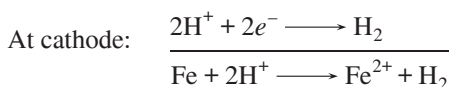
Substituting the given data in Nernst equation, we get

$$0.28 \text{ V} = 0.763 \text{ V} - \frac{0.05915 \text{ V}}{2} \log \frac{(0.1)(1)}{([\text{H}^{+}]/\text{mol dm}^{-3})^2}$$

$$\text{This gives} \quad -\log([\text{H}^{+}]/\text{mol dm}^{-3}) = \frac{1}{2} \left[ \frac{2(0.763 \text{ V} - 0.28 \text{ V})}{(0.05915 \text{ V})} - \log(0.1) \right] = \frac{1}{2} [16.33 + 1] = 8.67$$

Thus, the pH of the solution is 8.67.

6. At anode:  $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^{-}$



$$\text{Here} \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^{+}]^2}$$

$$E_{\text{cell}}^{\circ} = 0.00 \text{ V} - (-0.44 \text{ V}) = 0.44 \text{ V}$$

Substituting  $[\text{Fe}^{2+}] = 1 \times 10^{-3} \text{ M}$ ,  $[\text{H}^{+}] = 1 \times 10^{-2} \text{ M}$ ,  $n = 2$  and  $E_{\text{cell}}^{\circ} = 0.44 \text{ V}$  in expression (i), we get

$$E_{\text{cell}} = 0.44 - \frac{0.059}{2} \log \frac{10^{-3}}{(10^{-2})^2}$$

$$E_{\text{cell}} = 0.44 - 0.0295 \log 10 = 0.44 - 0.0295$$

$$E_{\text{cell}} = 0.4105 \text{ V}$$

$$E_{\text{cell}} = 0.41 \text{ V}$$

7.  $\text{A}^{2+} + \text{B}^{+} \rightarrow \text{A}^{3+} + \text{B}$ ;  $n = 1$

Substituting  $K_c = 10^{10}$ ,  $1 F = 96500 \text{ C mol}^{-1}$ ,  $T = (25 + 273) \text{ K}$ ,  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  in the expression

$$\Delta G^{\circ} = -2.303 RT \log K_c, \text{ we get}$$

$$\Delta G^{\circ} = -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log 10^{10}$$

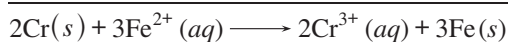
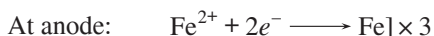
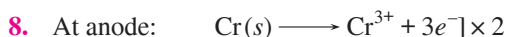
$$\Delta G^{\circ} = -57058.48 \text{ J mol}^{-1} = -57.058 \text{ kJ mol}^{-1}$$

Substituting  $\Delta G^{\circ} = -57058.48 \text{ J mol}^{-1}$ ,  $F = 96500 \text{ C mol}^{-1}$ ,  $n = 1$ , in the expression

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}, \text{ we get}$$

$$-57058.48 = -1 \times 96500 E_{\text{cell}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = \frac{57058.48}{96500} = 0.591 \text{ V}$$



$$E_{\text{cell}}^{\circ} = E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} - E_{\text{Cr}^{3+}/\text{Cr}}^{\circ}$$

$$= -0.44 \text{ V} - (-0.74 \text{ V})$$

$$E_{\text{cell}}^{\circ} = 0.30 \text{ V}$$

Here,  $n = 6$ ,  $E_{\text{cell}}^{\circ} = 0.30 \text{ V}$ ,  $[\text{Fe}^{2+}] = 0.1 \text{ M}$ ,  $[\text{Cr}^{3+}] = 0.01 \text{ M}$

Substituting these values in the Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}, \text{ we get}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{6} \log \frac{(10^{-2})^2}{(10^{-1})^3}$$

$$= 0.30 + 0.0098 \log 10$$

$$= 0.30 + 0.0098$$

$$E_{\text{cell}} = 0.3098 \text{ V}$$



Here,  $n = 2$

$$\log K_c = \frac{n}{0.059} E_{\text{cell}}^{\circ}$$

$$\log K_c = \frac{2}{0.059} \times 1.05 = 35.5$$

$$K_c = \text{antilog } 35.5 = 3.4 \times 10^{35}$$

$$K_c = 3.4 \times 10^{35}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G^{\circ} = -2 \times 96500 \times 1.05 = -202650 \text{ J}$$

$$\Delta G^{\circ} = -202.65 \text{ kJ}$$



$$\alpha = 95\%$$

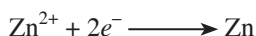
$$T = 298 \text{ K}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

$$[\text{Zn}^{2+}] = 0.1 \times \frac{95}{100}$$

$$= 0.095 \text{ M}$$

The cell reaction will be,



By Nernst equation

$$\begin{aligned}
 E_{\text{Zn}^{2+}/\text{Zn}} &= E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} - \frac{0.0591}{2} \log \left( \frac{1}{[\text{Zn}^{2+}]} \right) \\
 &= -0.76 - \frac{0.0591}{2} \log \left( \frac{1}{0.095} \right) \\
 &= -0.76 - \frac{0.0591}{2} \times 1.0223 \\
 &= -0.7902 \text{ V}
 \end{aligned}$$

## CHAPTER-2 Chemical kinetics

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1. No, the molecularity can never be equal to zero or a fractional number. Molecularity is the number of molecules involved in each elementary reaction which may be different, *i.e.*, the molecularity of each step may be different.

2. (i) For the first-order reaction, we have

$$k = -\frac{2.303}{t} \log \frac{[\text{A}]}{[\text{A}]_0} = -\frac{2.303}{(10 \text{ min})} \log \frac{80}{100} = 0.0223 \text{ min}^{-1}$$

$$(ii) t = -\frac{2.303}{k} \log \frac{[\text{A}]}{[\text{A}]_0} = -\frac{2.303}{(0.0223 \text{ min}^{-1})} \log \frac{25}{100} = 62.18 \text{ min.}$$

3. (i) Let  $a$  and  $b$  be the orders of the reaction with respect to  $A$  and  $B$ , respectively. We will have

$$r_0 = k[\text{A}]_0^a [\text{B}]_0^b$$

Making use of the second and third data in the given table, we get

$$4.0 \times 10^{-3} \text{ M s}^{-1} = k [5.0 \times 10^{-4} \text{ M}]^a [6.0 \times 10^{-5} \text{ M}]^b$$

$$1.6 \times 10^{-2} \text{ M s}^{-1} = k [1.0 \times 10^{-3} \text{ M}]^a [6.0 \times 10^{-5} \text{ M}]^b$$

Dividing the two expressions, we get

$$\frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = \left[ \frac{1.0 \times 10^{-3}}{5.0 \times 10^{-4}} \right]^a \quad \text{i.e. } 4 = 2^a$$

Hence,  $a = 2$

From the first and second data, we write

$$5.0 \times 10^{-4} \text{ M s}^{-1} = k [2.5 \times 10^{-4} \text{ M}]^2 [3.0 \times 10^{-5} \text{ M}]^b$$

$$4.0 \times 10^{-3} \text{ M s}^{-1} = k [5.0 \times 10^{-4} \text{ M}]^2 [6.0 \times 10^{-5} \text{ M}]^b$$

Dividing these two expressions, we get

$$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \left[ \frac{5.0 \times 10^{-4}}{2.5 \times 10^{-4}} \right]^2 \left[ \frac{6.0 \times 10^{-5}}{3.0 \times 10^{-5}} \right]^b \quad \text{i.e. } 8 = 2^2 2^b$$

Hence,  $b = 1$

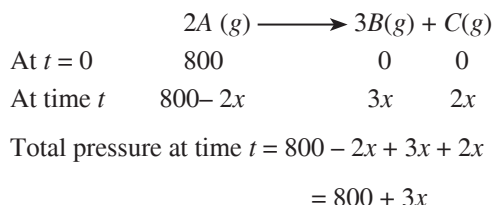
$$(ii) \text{ The rate constant } k \text{ is } = \frac{r_0}{[\text{A}]_0^2 [\text{B}]_0}$$

From the first data 300 K, we get

$$k = \frac{5.0 \times 10^{-4} \text{ M s}^{-1}}{(2.5 \times 10^{-4} \text{ M})^2 (3.0 \times 10^{-5} \text{ M})} = 2.67 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$$

4. (i) Data shows that half life ( $t_{1/2}$ ) of the given reaction is constant, i.e. 100 min. Hence, it is first order reaction.

(ii)  $t_{75}$ , i.e.,  $t_{3/4} = 2 \times t_{1/2}$   
 $= 2 \times 100$   
 $= 200 \text{ min}$



As given pressure of A = 700 mm Hg

So,  $800 - 2x = 700$   
 $800 - 700 = 2x$   
 $100 = 2x$   
 $x = 50$

Hence, total pressure will be  $800 + 3 \times 50 = 800 + 150 = 950 \text{ mm Hg}$

5. (i) (a) **Order of Reaction:** It may be defined as the sum of powers of the concentration of the reactants in the rate law expression.

(b) The rate of reaction when the molar concentration of each of the reactants is taken as unity is called rate constant. Its value depends on the temperature but independent of the concentration of reactions.

(ii)  $[R] = [R]_0 - 25\% \text{ of } [R]_0 = [R]_0 - \frac{25 \times [R]_0}{100} = \frac{3[R]_0}{4}$

Substituting  $[R] = \frac{3[R]_0}{4}$ ,  $t = 10 \text{ min}$ , in the expression  $k = \frac{2.303}{10} \log \frac{[R]_0}{[R]}$ , we get

$$k = \frac{2.303}{10} \log \frac{[R]_0}{[R]} = \frac{2.303}{10} \log \frac{4}{3}$$

$$k = \frac{2.303}{10} (\log 4 - \log 3) = \frac{2.303}{10} (0.6021 - 0.4771)$$

$$k = 0.02879 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.02879 \text{ min}^{-1}} = 24.07 \text{ min}$$

6. (i) Let Rate =  $k[A]^m [B]^n$
- $\therefore 1.5 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} = k(0.10)^m (0.10)^n$  ... (i)
- $3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} = k(0.2)^m (0.2)^n$  ... (ii)
- $6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} = k(0.2)^m (0.4)^n$  ... (iii)

Dividing equation (iii) by (ii), we get

$$\frac{6.0 \times 10^{-3}}{3.0 \times 10^{-3}} = \frac{k(0.2)^m (0.4)^n}{k(0.2)^m (0.2)^n}$$

$$2 = 2n \Rightarrow n = 1$$

Dividing equation (ii) by (i) we get

$$\frac{3.0 \times 10^{-3}}{1.5 \times 10^{-3}} = \frac{k(0.2)^m (0.2)^n}{k(0.1)^m (0.1)^n}$$

$$2 = 2^m 2^n \Rightarrow 2^{m+n} = 2^0 \cdot 2$$

$$2^m = 1 \text{ or } 2^m = 2^0 \Rightarrow m = 0$$

$$\text{Rate} = k[A]^0 [B]^1 \text{ or Rate} = k[B]$$

(ii)  $k = \frac{\text{Rate}}{[B]}$

$$k = \frac{1.5 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}}{0.1 \text{ mol L}^{-1}} = 1.5 \times 10^{-2} \text{ min}^{-1}$$

(c) The reaction mechanism (II) is consistent with the rate law found in (a).

7. As the reaction is of first order with respect to A and of second order w.r.t B.

$$\text{Rate of Reaction } (R_1) = k[A] [B]^2 \quad \dots(i)$$

Now, if the concentration of both A and B are doubled together the rate of reaction will become.

$$\text{Rate of reaction } (R_2) = k[2A] [2B]^2 \quad \dots(ii)$$

By dividing eq. (i) and (ii) we get.

$$\frac{R_1}{R_2} = \frac{k[A][B]^2}{k[2A][2B]^2}$$

$$\frac{R_1}{R_2} = \frac{1}{2 \times 4}$$

$$\frac{R_1}{R_2} = \frac{1}{8}$$

Hence,  $R_2 = 8R_1$

8. For the reaction  $R \xrightarrow{k} P$

$$\text{rate} = \frac{-d[R]}{dt} = k$$

$$d[R] = -k dt$$

Integrating both sides,

$$[R] = -kt + C, \quad \text{where } C = \text{constant of integration} \quad \dots(i)$$

At  $t = 0$ ,  $[R] = [R]_0$

Substituting this in equation (i)

$$C = [R]_0$$

Substituting the value of C in equation (i)

$$[R] = -kt + [R]_0 \quad \dots(ii)$$

$$kt = [R]_0 - [R]$$

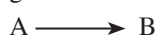
$$\Rightarrow t = \frac{[R]_0 - [R]}{k}$$

On completion of reactions,  $[R] = 0$

$$\therefore t = \frac{[R]_0}{k}$$

9. (i) The probability of more than three molecules collision is simultaneously very small. Hence possibility of molecularly being three is very low.

(ii) The given reaction is



Let, the initial rate is given by

$$r = k[A]^n \quad (i)$$

Where  $n$  is order of reaction.

Now, according to the question rate of reaction becomes three times as the concentration of A is increased by 9 times.

$$\text{i.e } 3r = k[9A]^n \quad (ii)$$

By dividing (ii) by (i), we get

$$\frac{3r}{r} = \frac{k[9A]^n}{k[A]^n}$$

$$\frac{3r}{r} = \frac{9^n k[A]^n}{k[A]^n}$$

$$3 = 9^n$$

$$3^1 = (3)^{2n}$$

$$2n = 1$$

$$n = \frac{1}{2} \quad \text{So, order of reaction is } \frac{1}{2}.$$

10. Given, rate constant ( $k$ ) =  $0.0051 \text{ min}^{-1}$

$$t = 3\text{h or } 180 \text{ m}$$

The integrated rate equation for first order reaction is

$$t = \frac{2.303}{R} \log \frac{[R]_0}{[R]}$$

$$180 = \frac{2.303}{.0051} \log \frac{[0.10]}{[R]}$$

$$\log \frac{0.1}{[R]^2} = \frac{180 \times .0051}{2.303} = \frac{918}{2303}$$

$$\log \frac{0.1}{[R]} = 0.3986$$

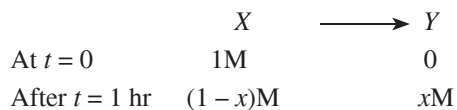
$$\frac{0.1}{[R]} = \text{Anti log } (0.3986)$$

$$= 2.503$$

$$[R] = \frac{0.1}{2.503} = 0.03995 \text{ M}$$

$$[R] = 0.04 \text{ M}$$

11. The given reaction is



So, rate of reaction after 1h =  $k(1-x)$  ... (i)

Now for first order reaction integrated rate equation is

$$k = \frac{2.303}{t} \log_{10} \frac{[R]_0}{R}$$

$$\text{or } 4.5 \times 10^{-3} = \frac{2.303}{1 \times 60} \log_{10} \frac{1}{1-x}$$

$$\log_{10} \frac{1}{1-x} = \frac{4.5 \times 10^{-3} \times 1 \times 60}{2.303}$$

$$\log_{10} \frac{1}{1-x} = 0.1172$$

$$\frac{1}{1-x} = \text{anti log } 0.1172$$

$$\frac{1}{1-x} = 1.310$$

$$(1-x) = 0.7633$$

Rate of reaction after 1 hr

$$= 4.5 \times 10^{-3} \times 0.7633$$

$$= 3.435 \times 10^{-3} \text{ M min}^{-1}$$

**12.** A + B  $\longrightarrow$  Products

Suppose order of reaction w.r.t reactant A is  $m$  and order of reaction w.r.t reactant B is  $n$ , then the rate law will be

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

Substituting the values 1 to 3 (from the given table) in the rate expression, we get.

$$0.05 = k(0.1)^m (0.1)^n \dots(i)$$

$$0.10 = k(0.2)^m (0.1)^n \dots(ii)$$

$$0.05 = k(0.1)^m (0.2)^n \dots(iii)$$

Dividing equation (ii) by (i), we get

$$\frac{0.1}{0.05} = \frac{k(0.2)^m (0.1)^n}{k(0.1)^m (0.1)^n} \text{ or } 2^1 = 2^m$$

$$\Rightarrow m = 1$$

Dividing equation (iii) by (i), we get

$$\frac{0.05}{0.05} = \frac{k(0.1)^m (0.2)^n}{k(0.1)^m (0.1)^n} \text{ or } 1 = 2^n \text{ or } 2^0 = 2^n$$

$$\Rightarrow n = 0$$

$$\therefore \text{Rate} = k [\text{A}]^1 [\text{B}]^0 \text{ or Rate} = k [\text{A}]$$

Overall order of reaction = 1

$$k = \frac{[\text{Rate}]}{[\text{A}]} \text{ or } k = \frac{0.05 \text{ mol L}^{-1} \text{ s}^{-1}}{0.1 \text{ mol L}^{-1}} \text{ or } k = 0.5 \text{ s}^{-1}$$

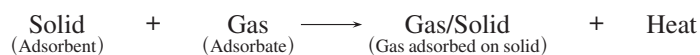
$$\text{For a first order reaction, } t_{1/2} = \frac{0.693}{k}$$

$$\therefore t_{1/2} = \frac{0.693}{0.5 \text{ s}^{-1}} = 1.386 \text{ s}$$

## CHAPTER-3 Surface Chemistry

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1. Gold sol which is lyophobic starts behaving like a lyophilic colloid when gelatin is added to it.
2. (i) As physisorption is an exothermic process:



According to Le Chatelier's principle, if we increase the temperature, equilibrium will shift in the backward direction, *i.e.*, gas is released from the adsorbed surface.

(ii) Clouds are colloidal in nature and carry charge. By throwing of common salt, an electrolyte on the



- clouds, results in coagulation leading to artificial rain.
3. (i) Because of larger area of colloidal gold and easy assimilation with the blood which is colloidal is used for inter molecular injection.  
(ii) Charges leads to the effect of repulsion, causing the precipitate particles to disperse forming a colloid.  
(iii) Finely divided substance is more effective as an adsorbent because finely divided substance provides more surface for adsorption.
  4. (i) **Macromolecular colloids:** Macromolecules in suitable solvents form solutions, where size of the macromolecules may fall within the colloidal range. The system showing such characteristics are called macromolecular colloids. The colloids are quite stable and in many respect they resemble true solutions. Examples of naturally occurring macromolecules are starch, cellulose, proteins and those of man-made macromolecules are nylon, polythene, polystyrene, synthetic rubber, etc.  
**Multimolecular colloids:** A large number of atoms or smaller molecules (diameter < 1 nm) of a substance on dissolution aggregate together to form species having size in the colloidal range. Such species are called multimolecular colloids. Examples: a sulphur sol consist of particles containing thousands of S<sub>8</sub> sulphur molecules, a platinum or gold sol may have particles of various sizes having many atoms.  
(ii) **Peptization and Coagulation:** Coagulation is the process of setting of colloidal particles whereas peptization is the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small electrolyte having a common ion.  
(iii) **Electrophoresis and electro dialysis**  
**Electrophoresis:** The movement of colloidal particles towards oppositely charged electrode in an electric field is called electrophoresis. If the movement of colloidal particles takes place towards the cathode, the phenomenon is called cataphoresis.  
**Electrodialysis:** The process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane by applying an electric field is called electro dialysis.
  5. River water is a colloidal solution of clay and sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in the sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.
  6. Yes. Clouds are colloidal in nature and carry charge. Spray of silver iodide, an electrolyte, results in coagulation leading to rain.
  7. BaCl<sub>2</sub>, Ba<sup>2+</sup> ion has greater coagulating power than K<sup>+</sup> ion as Ba<sup>2+</sup> ion has higher charge.
  8. 
$$\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \longrightarrow \underset{\text{(Yellow sol)}}{\text{As}_2\text{S}_3} + 3\text{H}_2\text{O}$$
  9. Colloidal solutions exhibit Tyndall effect because the size of the colloidal particles (1 nm–1000 nm) is such that they can scatter light.
  10. Unbalanced bombardment of the particles of dispersed phase by molecules of dispersion medium causes Brownian motion. This stabilizes the solution.

## CHAPTER–4 *d* & *f* block elements

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1. Lanthanoids are called *f*-block elements because the last electrons in them enters into *f*-orbital.
2. Cerium (Z = 58) exhibits +4 oxidation state.
3. (i) This is because in presence of complexing reagents, the CFSE value is more that compensates the third ionisation energy of cobalt.  
(ii) The ions with *d*<sup>1</sup> configuration have the tendency to lose the only electron present in *d*-subshell to acquire stable *d*<sup>0</sup> configuration. Therefore, they are unstable and undergo oxidation or disproportionation.

4. Electronic configuration of Cr atom with  $Z = 24$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

$\therefore$  Electronic configuration of  $\text{Cr}^{3+} = [\text{Ar}] 3d^3$



Hence, it has three unpaired electrons.

$\therefore$  Spin only magnetic moment ( $\mu$ )

$$= \sqrt{n(n+2)} \text{ BM}$$

$$= \sqrt{3(3+2)} \text{ BM}$$

$$= \sqrt{3(15)} \text{ BM}$$

$$= \sqrt{15} \text{ BM}$$

$$= 3.87 \text{ BM}$$

5. (i) The divalent ion in aqueous solution will have  $d^5$  configuration (five unpaired electrons) with atomic number 25. The magnetic moment  $\mu$  is

$$\mu = \sqrt{5(5+2)} \text{ BM} = 5.92 \text{ BM}$$

(ii) According to  $n+l$  rule:

For 3d orbital

$$n+l = 3+2 = 5$$

For 4s orbital

$$n+l = 4+0 = 4$$

As the value of  $n+l$  for 4s orbital is less than the 3d orbital, so we filled first as it has lower energy than 3d and ionisation enthalpy is responsible for the ionisation of atom, 4s electrons are loosely held by the nucleus. Therefore electrons are removed from 4s orbital prior to 3d orbital.

6. (i) The elements which contain incompletely filled  $d$  orbitals in the ground state or in the oxidised state can show following properties:

(a) They can form complex compounds.

(b) They show variable oxidation state.

(c) They are used as catalyst.

(ii) The elements which contribute more valence electrons per atom in the formation of metallic bonds show following properties:

(a) They are hard.

(b) They have high melting and boiling point.

(c) They have high enthalpy of atomization.

(d) They are malleable and ductile

7. (i) The main reason for positive  $E^0$  (0.34 V) value for copper is that the sum of enthalpies for sublimation and ionization is not balanced by hydration enthalpy.

(ii)  $\text{Cr}^{2+}$  is reducing as its configuration changes from  $d^4$  to  $d^3$ , a more stable half filled  $t_{2g}$  configuration while  $\text{Mn}^{3+}$  is oxidising as  $\text{Mn}^{3+}$  to  $\text{Mn}^{2+}$  results a more stable half filled  $d^5$  configuration.

(iii) The oxidising power of oxonions are in the order  $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$ , this is due to increase in the oxidation state of the metal ion.

8. (i) It is due to regular increase in ionisation enthalpy.

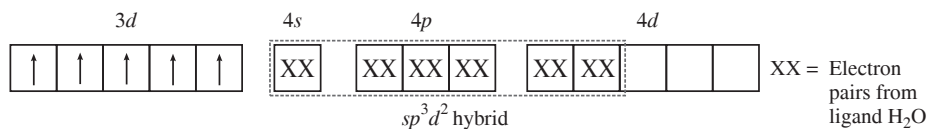
(ii)  $\text{Mn}^{2+}$  has the maximum paramagnetic character because of the maximum number of unpaired electrons, viz., 5.

(iii) Due to symmetrical electronic configuration there is no orbital contribution in  $\text{Cr}^{3+}$  ion. However, appreciable orbital contribution takes place in  $\text{Co}^{2+}$  ion.

9. (i)  $\text{Sc}^{3+} = 3d^0 4s^0$  (No unpaired electrons)  
 $\text{V}^{3+} = 3d^2 4s^0$  (2 unpaired electrons)  
 $\text{Ti}^{4f} = 3d^0 4s^0$  (No unpaired electrons)  
 $\text{Mn}^{2+} = 3d^5 4s^0$  (5 unpaired electrons)  
 Thus, only  $\text{V}^{3+}$  and  $\text{Mn}^{2+}$  are coloured because they have unpaired electrons.
- (ii) Out of  $\text{Mn}^{3+}$  and  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$  is more paramagnetic than  $\text{Cr}^{3+}$  because  $\text{Mn}^{3+}$  has four unpaired electrons in its valence shell while  $\text{Cr}^{3+}$  has three unpaired electrons.
10. (i) As the size decreases covalent character increases. Therefore,  $\text{La}_2\text{O}_3$  is more ionic and  $\text{Lu}_2\text{O}_3$  is more covalent.
- (ii) As the size decreases from La to Lu, stability of oxosalts also decreases.
- (iii) Stability of the complexes increases as the size of lanthanoids decreases.
- (iv) Radii of  $4d$  and  $5d$  block elements will be almost same.
- (v) Acidic character of oxides increases from La to Lu.

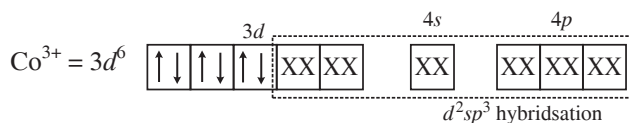
## CHAPTER-5 Coordination Compounds

1. (i)  $\text{Fe}^{3+}([\text{Ar}]3d^5)$



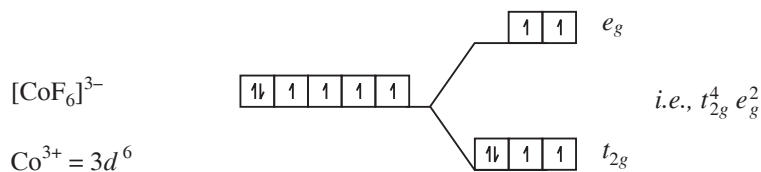
Hybridisation	$sp^3d^2$
Magnetic character	Paramagnetic
Spin of the complex	High spin complex

2.  $[\text{Co}(\text{NH}_3)_6]^{3+}$



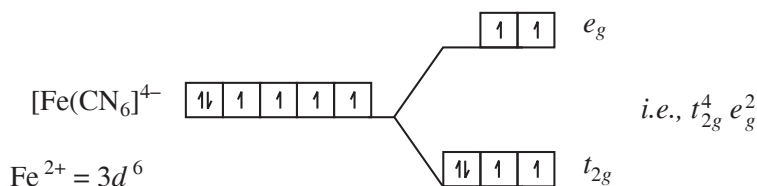
- (i)  $d^2sp^3$     (ii) Inner orbital complex    (iii) diamagnetic    (iv) zero

- 3.



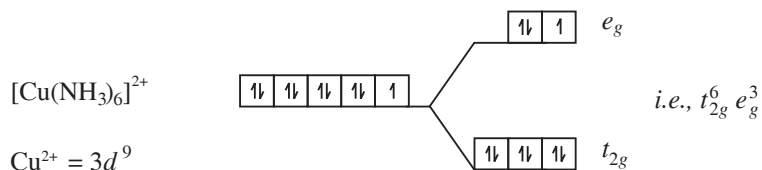
Number of unpaired electrons ( $n$ ) = 4

Magnetic moment =  $\sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9 \text{ BM}$



Number of unpaired electrons ( $n$ ) = 4

$$\text{Magnetic moment} = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9 \text{ BM}$$



Number of unpaired electrons ( $n$ ) = 1

$$\begin{aligned} \text{Magnetic moment} &= \sqrt{n(n+2)} \\ &= \sqrt{1(1+2)} \\ &= \sqrt{1 \times 3} \\ &= \sqrt{3} \\ &= 1.73 \text{ BM} \end{aligned}$$

4.  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2] \text{Cl}$ ; tetraaquadichloridochromium(III) chloride

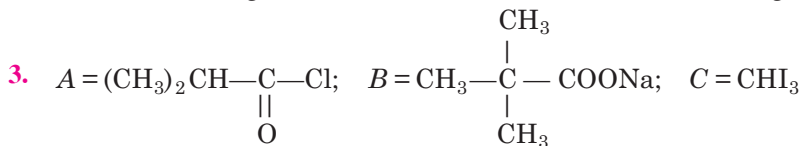
5. (i)  $\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$ ,  $\text{O}=\overset{\text{O}^-}{\underset{|}{\text{C}}}-\overset{\text{O}^-}{\underset{|}{\text{C}}}=\text{O}$
- (ii) CO is a stronger ligand than  $\text{Cl}^-$  as it is a  $\pi$ -acceptor ligand.
6. (i) In  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , the secondary valencies are 6.
- (ii) In  $\text{PtCl}_4 \cdot 2\text{HCl}$ , the secondary valencies are 6.
- (iii) In  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , the secondary valencies are 6.
7. Difference between double salt and coordination compound.

S.No.	Double Salt	Coordination Compound
(i)	These salts contains two simple salts in equimolar ratio.	These salts contains simple salts by they may or may not be in simple ratio.
(ii)	It loses their identity in the solution.	It retains its identity in the solution.

8. (i) It involves a number of assumptions.
- (ii) It does not give quantitative interpretation of magnetic data.
- (iii) It does not distinguish between weak and strong ligands.
- (iv) It does not explain the colour exhibited by complexes.
- (v) It does not give an exact explanation of thermodynamic or kinetic stabilities of coordination compounds.
- (vi) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinated complexes.
9.  $\Delta_t = \frac{4}{9} \Delta_0$
- $$\Delta_t = \frac{4}{9} \times 18,000 = 8000 \text{ cm}^{-1}$$
10. (i) As  $\Delta_0 > P$  pairing will occur in the  $t_{2g}$  orbitals and  $e_g$  orbitals will remain vacant.
- (ii)  $t_{2g}^4 e_g^0$
- (iii) As there are three bidentate ligands to combine therefore hybridisation will be  $d^2sp^3$ .

## CHAPTER-6 Aldehydes, Ketones and Carboxylic Acid

- Ethyl-4-chlorobenzoate
- Ethanol can undergo esterification whereas ethanol doesn't undergo the same reaction.



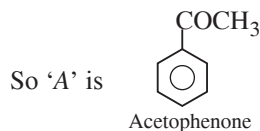
- Due to +R effect of benzene ring, the electron density in the carbonyl group of benzaldehyde increases. This in turn, increases the electron density in the C—H bond of aldehyde group. As a result, the C—H bond becomes stronger and hence only oxidising agent like Tollens' agent;  $\text{Ag}(\text{NH}_3)_2^+$  ( $E_{\text{Ag}^+/\text{Ag}}^0 = 0.8 \text{ V}$ ) can oxidise C—H to C—OH to form carboxylic acids but weaker oxidising agents like Fehling's solution or Benedict's solution ( $E_{\text{Cu}^{2+}/\text{Cu}^+}^0 = 0.18 \text{ V}$ ) fail to oxidise benzaldehyde to benzoic acid.

(ii) This is because  $(\text{CH}_3)_2\text{CHCHO}$  has one  $\alpha$ -hydrogen whereas  $(\text{CH}_3)_3\overset{\alpha}{\text{C}}-\text{CHO}$  does not have any.

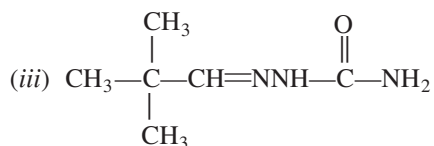
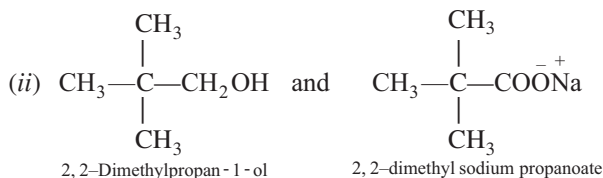
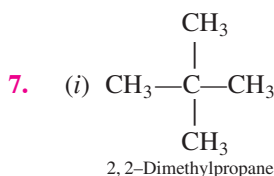
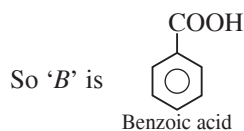
- Pyridinium chlorochromate ( $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$ ) or Cu at 573 K.

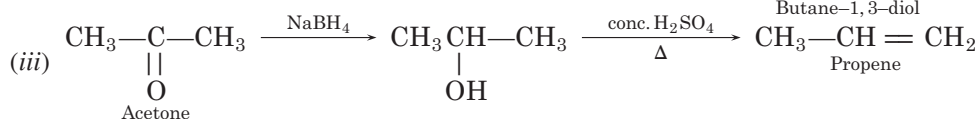
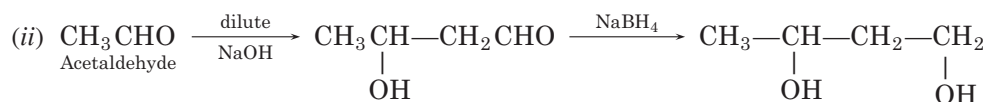
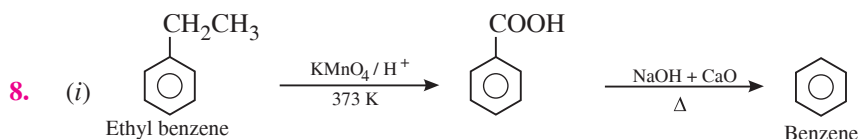
(ii)  $\text{NH}_3, \Delta$  (Heat)

- As 'A' does not give Fehling's or Tollens' test, so it does not have —CHO group but it gives positive iodoform test and DNP test so it has  $\text{CH}_3-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-$  group.

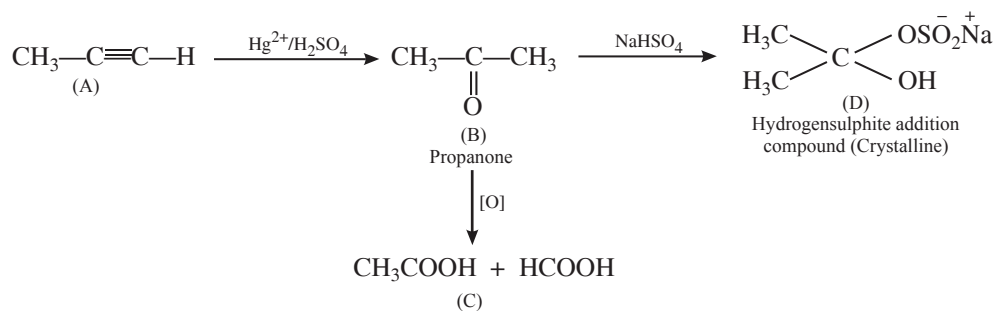


B is carboxylic acid obtained by oxidation of A with  $\text{H}_2\text{CrO}_4$ .



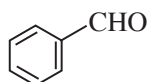


9.

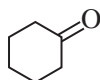


Compound B (propanone) is a ketone therefore Fehling's test and Tollens' tests are negative.

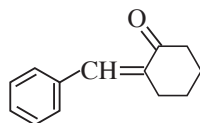
10.



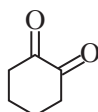
A = Benzaldehyde



B = Cyclohexanone



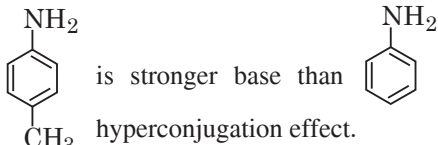
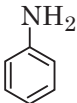
C = 2-Benzylidene cyclohexanone



D = Cyclohexane-1, 2-dione



- (ii)  $\text{CH}_3\text{NH}_2$  is more basic than  $\text{NH}_3$ .  $\text{CH}_3$  group due to its +ve I effect pushes electron towards nitrogen in  $\text{CH}_3\ddot{\text{N}}\text{H}_2$  and this makes the unshared electron pair more available for sharing with the proton of the acid.

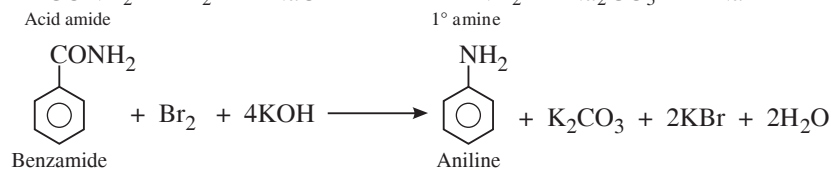
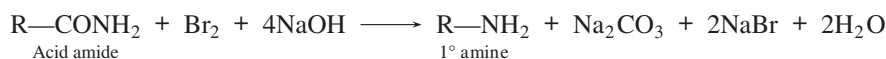
- (iii)  is stronger base than  as  $\text{CH}_3$  group is electron releasing by +I effect and hyperconjugation effect.

8. (i) Due to resonance the lone pair of electrons on nitrogen of acetanilide gets delocalised towards carbonyl group.

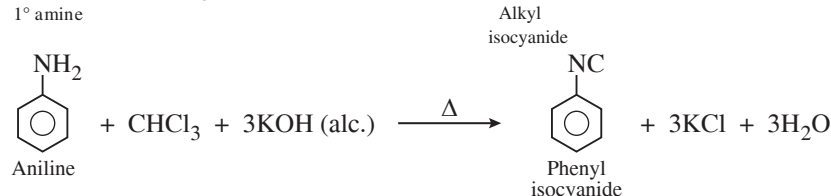
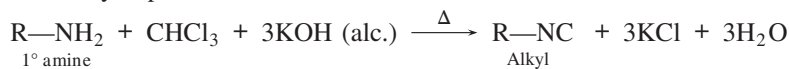


Hence the electrons are less available for donation to benzene ring by resonance. Therefore, activation effect of aniline is reduced.

- (ii) In  $\text{CH}_3\text{—NH}_2$ , +I-effect of  $\text{—CH}_3$  group increases the electron density on the nitrogen atom making lone pair more available for donation. On the other hand, in aniline lone pair of electron on the nitrogen atom is delocalised over benzene ring due to resonance and thus making it less available for donation. That is why  $\text{CH}_3\text{NH}_2$  is more basic than  $\text{C}_6\text{H}_5\text{NH}_2$ .
- (iii) This is because in a strongly acidic medium aniline is protonated to form the anilinium ion which is meta directing.
9. (i) (a) **Hoffmann bromamide reaction:** When a primary acid amide is heated with an aqueous or ethanolic solution of NaOH or KOH and bromine (*i.e.*, NaOBr or KOBr), it gives a primary amine with one carbon atom less.



- (b) **Carbylamine reaction (Isocyanide test):** Aliphatic and aromatic primary amines when heated with chloroform and alcoholic solution of KOH give isocyanides (carbylamines) which have extremely unpleasant smell.



- (ii) Aniline when react with  $\text{HNO}_2$  at 273 – 278K followed by treatment with an alkaline solution of 2-naphthol, by treatment with an alkaline solution of 2-naphthol, where a brilliant yellow, orange or red coloured dye is obtained. While methyl amine under these conditions give a brisk evolution of  $\text{N}_2$  gas with the formation of primary alcohols. *i.e.* the solution remains clear.



10.

