# NUMERICAL EXAMPLES

# Q. Solve the following examples : (1, 2 or 3 marks each)

[Note : In the question paper, Section–A carries two numerical type MCQs and one simple numerical of one mark each. Section–B carries two numericals each of two marks while Section–C carries two numericals each of three marks. Section–D has one numerical of two marks.]

## Chapter 1. Solid State

(1) In an ionic crystalline solid atoms of element Y form hcp lattice. The atoms of element X occupy one third of tetrahedral voids. What is the formula of the compound? (2 marks)

**Solution :** In the given hcp lattice, Y atoms are present at 12 corners and 2 face centres.

 $\therefore$  Number of Y atoms  $=\frac{1}{6} \times 12 + 2 \times \frac{1}{2} = 3$ 

There are 6 tetrahedral voids, hence the number of X atoms

$$=\frac{1}{3}\times 6=2$$

 $\therefore$  Formula of the compound is  $X_2Y_3$ .

(2) The density of iridium is 22.4 g/cm<sup>3</sup>. The unit cell of iridium is fcc. Calculate the radius of iridium atom. Molar mass of iridium is 192.2 g/mol. *(3 marks)* 

Solution : Given : Crystal structure of iridium = fcc

Molar mass of iridium =  $192.2 \text{ gmol}^{-1}$ 

Density =  $\rho = 22.4 \text{ gcm}^{-3}$ 

Radius of iridium = ?

In fcc structure, there are 8 Ir atoms at 8 corners and 6 Ir atoms at 6 face centres.

 $\therefore \text{ Total number of Ir atoms} = \frac{1}{8} \times 8 + \frac{1}{2} \times 6$ = 1 + 3 = 4

Mass of Ir atom =  $\frac{192.2}{6.022 \times 10^{23}}$  = 31.92 × 10<sup>-23</sup> g ∴ Mass of 4 Ir atoms = 4 × 31.92 × 10<sup>-23</sup> g = 1.277 × 10<sup>-21</sup> g ∴ Mass of unit cell = 1.277 × 10<sup>-21</sup> g Density of unit cell =  $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$ 22.4 =  $\frac{1.277 \times 10^{-21}}{a^3}$ ∴  $a^3 = \frac{1.277 \times 10^{-21}}{22.4} = 57 \times 10^{-24} \text{ cm}^3$ ∴  $a = (57 \times 10^{-24})^3 = 3.848 \times 10^{-8} \text{ cm}$ If *r* is the radius of iridium atom, then for fcc structure,

$$r = \frac{a}{2\sqrt{2}} = \frac{3.848 \times 10^{-8}}{2 \times 1.414} = 1.36 \times 10^{-8} \text{ cm} = 136 \text{ pm}$$

Ans. Radius of iridium atom = 136 pm.

(3) One mole of an ideal gas is expanded isothermally and reversibly from 10 L to 15 L at 300 K. Calculate the work done in the process. (2 marks)

**Solution :** 

Given : 
$$n = 1 \mod$$
,  $V_1 = 10 \text{ L}$ ,  $V_2 = 15 \text{ L}$ ,  $T = 300 \text{ K}$ ,  $W_{\text{max}} = ?$   
 $W_{\text{max}} = -2.303 \ nRT \log_{10} \frac{V_2}{V_1}$   
 $= -2.303 \times 1 \times 8.314 \times 300 \times \log_{10} \frac{15}{10}$   
 $= -1011.5 \text{ J}$   
 $= -1.0115 \text{ kJ}$ 

Ans.  $W_{\text{max}} = -1.0115$  kJ.

(4) Aluminium crystallizes in cubic close packed structure with unit cell edge length of 353.6 pm. What is the radius of Al atom ? How many unit cells are there in 1.00 cm<sup>3</sup> of Al ? *(3 marks)* 

Solution : Given : Structure of Al = Cubic close packed structure

$$= ccp structure$$

Edge length of unit cell = a = 353.6 pm  $=3.536 \times 10^{-8}$  cm r = ?, Number of unit cells in 1.00 cm<sup>3</sup> of Al = ? Radius of Al atom =  $r = \frac{a}{2\sqrt{2}} = \frac{353.6}{2\sqrt{2}}$  $=\frac{353.6}{2 \times 1.414} = 125 \text{ pm}$ Volume of one unit cell =  $a^3 = (3.536 \times 10^{-8})^3$  $=4.421 \times 10^{-23} \text{ cm}^3$ Number of unit cells =  $\frac{1.00}{4.421 \times 10^{-23}} = 2.26 \times 10^{22}$ Ans. Radius of Al atom = 125 pmNumber of unit cells =  $2.26 \times 10^{22}$ . (5) A compound forms hexagonal close packed (hcp) structure. What is the number of (i) octahedral voids (ii) tetrahedral voids (iii) total voids formed in 0.4 mole of it? (3 marks) **Solution :** Structure = hcp; n = 0.4 mol, Octahedral voids = ?, Tetrahedral voids =?, Total voids =? Number of atoms =  $n \times N_A$  $= 0.4 \times 6.022 \times 10^{23}$  $= 2.4088 \times 10^{23}$ (i) Number of octahedral voids = Number of atoms  $= 2.4088 \times 10^{23}$ (ii) Number of tetrahedral voids  $= 2 \times \text{Number of atoms}$  $= 2 \times 24088 \times 10^{23}$  $=4.8176 \times 10^{23}$  $\simeq 4.818 \times 10^{23}$ (iii) Total number of voids =  $2.4088 \times 10^{23} + 4.818 \times 10^{23}$  $= 7.2268 \times 10^{23}$  $\simeq 7.227 \times 10^{23}$ Ans. (i) Number of octahedral voids =  $2.4088 \times 10^{23}$ (ii) Number of tetrahedral voids =  $4.818 \times 10^{23}$ (iii) Total number of voids =  $7.227 \times 10^{23}$ .

(6) Gold crystallizes into face-centred cubic cells. The edge length of unit cell is  $4.08 \times 10^{-8}$  cm. Calculate the density of gold.

[Molar mass of gold = 197 g mol<sup>-1</sup>] (3 marks) Solution : Given : Crystal = fcc; Edge length =  $a = 4.08 \times 10^{-8}$  cm, Molar mass = M = 197 g mol<sup>-1</sup>, Number of atoms in unit cell = n = 4,  $\rho = ?$ 

$$\rho = \frac{n \times M}{a^3 \times N_A}$$
  
=  $\frac{4 \times 197 \text{g mol}^{-1}}{(4.08 \times 10^{-8})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}$   
= 19.27 g cm<sup>-3</sup>

**Ans.** Density = 19.27 g cm  $^{-3}$ .

(7) Calculate the number of atoms and unit cell present in 0.5 g of Niobium if it forms body-centred cubic structure. The density of Niobium is 8.55 g cm<sup>-3</sup> and edge length of unit cell is 330.6 pm.

(3 marks)

Solution : Given : Mass of Nb = 0.5g; Unit cell = bcc;  $\rho = 8.55 \text{ g cm}^{-3}$ ;  $a = 330.6 \text{ pm} = 3.306 \times 10^{-8} \text{ cm}$ For bcc, n = 2Number of atoms = ?, Number of unit cells = ?  $\rho = \frac{n \times M}{a^3 \times N_A}$   $\therefore M = \frac{\rho \times a^3 \times N_A}{n}$   $= \frac{8.55 \times (3.306 \times 10^{-8})^3 \times 6.023 \times 10^{23}}{2} = 93 \text{ g mol}^{-1}$ Number of Nb atoms  $= \frac{0.5}{93} \times 6.023 \times 10^{23} = 3.328 \times 10^{21}$ Each bcc unit cell contains 2 atoms  $\therefore$  Number of unit cells  $= \frac{3.328 \times 10^{21}}{2} = 1.664 \times 10^{21}$ Ans. (a) Number of Nb atoms  $= 3.328 \times 10^{21}$ . (b) Number of unit cells  $= 1.664 \times 10^{21}$ .

## Additional Important Examples for Self-practice

- **1.** A compound is formed by two elements A and B. The atoms of element B forms ccp structure. The atoms of A occupy 1/3rd of tetrahedral voids. What is the formula of the compound ?(**Ans.** A<sub>2</sub>B<sub>3</sub>)
- When gold crystallizes, it forms face-centred cubic cells. The unit cell edge length is 408 pm. Calculate the density of gold. Molar mass of gold is 197 g/mol. (Ans. 19.27 g cm<sup>-3</sup>, 19.27 × 10<sup>3</sup> kg dm<sup>-3</sup>)
- 3. A compound made of elements C and D crystallizes in fcc structure. Atoms of C are present at the corners of the cube. Atoms of D are at the centres of faces of the cube. What is the formula of the compound ? (Ans. Formula of compound = CD<sub>3</sub>)
- 4. The unit cell of metallic silver is fcc. If radius of Ag atom is 144.4 pm, calculate (a) edge length of unit cell (b) volume of Ag atom (c) the per cent of the volume of a unit cell, that is occupied by Ag atoms (d) the per cent of empty space.

[**Ans.** (a)  $a = 4.085 \times 10^{-8}$  cm)

(b) Volume of Ag atom =  $1.261 \times 10^{-23} \text{ cm}^3$ 

(c) Per cent of volume occupied by Ag atoms = 74%

(d) Per cent of empty space = 26%]

5. Niobium forms bcc structure. The density of niobium is  $8.55 \text{ g/cm}^3$  and length of unit cell edge is 330.6 pm. How many atoms and unit cells are present in 0.5 g of niobium?

(Ans. Number of unit cells =  $1.62 \times 10^{21}$ )

**6.** A compound forms hcp structure. What is the number of (a) octahedral voids (b) tetrahedral voids (c) total voids formed in 0.4 mol of it?

[Ans. (a) Number of octahedral voids =  $2.4098 \times 10^{23}$ 

(b) Number of tetrahedral voids =  $4.8196 \times 10^{23}$ 

(c) Total number of voids =  $7.229 \times 10^{23}$ ]

- 7. If the density of a crystalline element having atomic mass 50 is  $6.8 \text{ g cm}^{-3}$  and the crystalline structure is body-centred cubic, find the edge length. (Ans. 290 pm)
- 8. When gold crystallizes, it forms face-centred cubic cells. The unit cell edge length is 408 pm. Calculate the density of gold. Molar mass of gold is 197 g/mol. (Ans. 19.27 g cm<sup>-3</sup>, 197g/mol)

(1) Fish generally needs  $O_2$  concentration in water at least 3.8 mg/L for survival. What partial pressure of  $O_2$  above the water is needed for the survival of fish? Given the solubility of  $O_2$  in water at 0 °C and 1 atm partial pressure is  $2.2 \times 10^{-3}$  mol/L. (2 marks) Solution : Given :

Required concentration of  $O_2 = 3.8 \text{ mg/L} = \frac{3.8 \times 10^{-3}}{32} \text{ mol L}^{-1}$ Solubility of  $O_2 = 2.2 \times 10^{-3} \text{ mol L}^{-1}$  P = 1 atmPartial pressure of  $O_2$  needed =  $Po_2 = ?$   $S = K_H \times Po_2$   $\therefore K_H = \frac{S}{Po_2} = \frac{2.2 \times 10^{-3}}{1} = 2.2 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$  $\therefore Po_2 = \frac{S}{K_H} = \frac{3.8 \times 10^{-3}}{32} \times \frac{1}{2.2 \times 10^{-3}} = 0.05397 \text{ atm}$ 

Ans. Pressure needed =  $Po_2 = 0.05397$  atm.

(2) Henry's law constant for  $CH_3Br_{(g)}$  is 0.159 mol dm<sup>-3</sup> bar<sup>-1</sup> at 25 °C. What is solubility of  $CH_3Br_{(g)}$  in water at same temperature and partial pressure of 0.164 bar? (1 mark)

**Solution : Given :**  $K_{\rm H} = 0.159 \text{ mol } \text{dm}^{-3} \text{ bar}^{-1}$ ; P = 0.164 bar; S = ?

 $S = K_{\rm H} \times P = 0.159 \times 0.164 = 0.026 \,\,{\rm M}$ 

Ans. Solubility of  $CH_3Br = 0.026$  M.

(3) The vapour pressure of water at 20 °C is 17 mm Hg. Calculate the vapour pressure of a solution containing 2.8 g of urea (NH<sub>2</sub>CONH<sub>2</sub>) in 50 g of water. (2 marks)

Solution :

**Given :** Vapour pressure of pure solvent (water) =  $P_0 = 17$  mm Hg Weight of solvent =  $W_1 = 50$  g Weight of solute (urea) = 2.8 g Molecular weight of a solvent =  $M_1 = 18$ Molecular weight of a solute (urea) =  $M_2 = 60$  g mol<sup>-1</sup>  $\frac{P_0 - P}{P_0} = \frac{W_2 \times M_1}{W_1 \times M_2}$   $\therefore \frac{17 - P}{17} = \frac{2.8 \times 18}{50 \times 60} = 0.0168$  $\therefore 17 - P = 17 \times 0.0168$ 17 - P = 0.2856 $\therefore P = 17 - 0.2856 = 16.7144 \text{ mm Hg.}$ Ans. Vapour pressure of solution = 16.7144 mm Hg.

(4) The normal boiling point of ethyl acetate is 77.06 °C. A solution of 50 g of nonvolatile solute in 150 g of ethyl acetate boils at 84.27 °C. Evaluate the molar mass of solute if  $K_b$  for ethyl acetate is 2.77 K kg mol<sup>-1</sup>. (2 marks)

Solution : Given : 
$$T_0 = 77.06 + 273 = 350.06$$
 K  
 $T = 84.27 + 273 = 357.27$  K  
 $\Delta T_b = 357.27 - 350.06 = 7.21$  K  
 $K_b = 2.77$  K kg mol<sup>-1</sup>;  $W_1 = 150$  g;  $W_2 = 50$  g,  $M_2 = ?$   
 $\Delta T_b = K_b \times \frac{W_2 \times 1000}{W_1 \times M_2}$   
 $\therefore M_2 = \frac{K_b \times W_2 \times 1000}{W_1 \times \Delta T_b}$   
 $= \frac{2.77 \times 50 \times 1000}{150 \times 7.21}$   
 $= 128.1$  g mol<sup>-1</sup>

**Ans.** Molar mass =  $128.1 \text{ g mol}^{-1}$ .

(5) A 5% aqueous solution (by mass) of cane sugar (molar mass 342 g/mol) has freezing point of 271 K. Calculate the freezing point of 5% aqueous glucose solution. (2 marks)

Solution : Given : 
$$W_2 = 5$$
 g cane sugar;  $W_1 = 100 - 5 = 95$  g  
 $M_2 = 342$  g mol<sup>-1</sup>;  $T_{f_1} = 271$  K;  
 $\Delta T_{f_1} = 273 - 271 = 2$  K;  $T_f = ?$   
 $W_2 = 5$  g glucose,  $W'_1 = 100 - 5 = 95$  g,  
 $M'_2 = 180$  g mol<sup>-1</sup>,  $\Delta T_{f_2} = ?$   
 $\Delta T_{f_1} = K_f \times \frac{W_2 \times 1000}{W_1 \times M_2}$   
 $\therefore K_f = \frac{\Delta T_{f_1} \times W_1 \times M_2}{W_2 \times 1000} = \frac{2 \times 95 \times 342}{5 \times 1000}$   
 $= 12.996$  K kg mol<sup>-1</sup>  $\cong 13$  K kg mol<sup>-1</sup>

$$\Delta T_{f_2} = K_f \times \frac{W'_2 \times 1000}{W'_1 \times M'_2}$$
$$= \frac{13 \times 5 \times 1000}{95 \times 180}$$
$$= 3.801 \text{ K}$$

 $\therefore$  Freezing point of solution =  $T_f = 273 - 3.801 = 269.2$  K Ans. Freezing point of solution = 269.2 K.

(6) What is the molar mass of a solute if a solution prepared by dissolving 0.822 g of it in 0.3 dm<sup>3</sup> of water has an osmotic pressure of 0.196 atm at 298 K? (2 marks)

Solution : 
$$W_2 = 0.822$$
 g;  $V = 0.3$  dm<sup>3</sup>  
 $\pi = 0.196$  atm;  $T = 298$  K;  $M_2 = ?$   
 $\pi = \frac{W_2 \times R \times T}{M_2 \times V}$   
 $\therefore M_2 = \frac{W_2 \times R \times T}{\pi \times V}$   
 $= \frac{0.822 \times 0.08205 \times 298}{0.196 \times 0.3}$   
 $= 341.8$  g mol<sup>-1</sup>

Ans. Molar mass of solute =  $341.8 \text{ g mol}^{-1}$ .

(7) A mixture of benzene and toluene contains 30% by mass of toluene. At 30 °C, vapour pressure of pure toluene is 36.7 mm Hg and that of pure benzene is 118.2 mm Hg. Assuming that the two liquids form ideal solutions, calculate the total pressure and partial pressure of each constituent above the solution at 30 °C. *(3 marks)* 

**Solution : Given :** 30% by mass of toluene (T) and 70% by mass of benzene (B).

$$W_{\rm T} = 30 \text{ g}; W_{\rm B} = 70 \text{ g}$$
  
 $P_{\rm T}^0 = 36.7 \text{ mm Hg}; P_{\rm B}^0 = 118.2 \text{ mm Hg}$   
 $M_{\rm T} = 92 \text{ g mol}^{-1}; M_{\rm B} = 78 \text{ g mol}^{-1}$   
 $P_{\rm T} = ?; P_{\rm B} = ?; P_{\rm soln} = ?$   
 $n_{\rm T} = \frac{W_{\rm T}}{M_{\rm T}} = \frac{30}{92} = 0.3260 \text{ mol}$ 

$$n_{\rm B} = \frac{W_{\rm B}}{M_{\rm B}} = \frac{70}{78} = 0.8974 \text{ mol}$$

Total number of moles  $= n_{\text{Total}} = n_{\text{T}} + n_{\text{B}}$ 

$$= 0.326 + 0.8974 = 1.2234$$
 mol

Mole fractions :

 $x_{\rm T} = \frac{n_{\rm T}}{n_{\rm Total}} = \frac{0.326}{1.2234} = 0.2665$   $x_{\rm B} = 1 - 0.2665 = 0.7335$   $P_{\rm soln} = x_{\rm T} + P_{\rm T}^{0} + x_{\rm B} \times P_{\rm B}^{0}$   $= 0.2665 \times 36.7 + 0.7335 \times 118.2$  = 9.780 + 86.7 = 96.48 mm HgPartial pressures :  $P_{\rm T} = x_{\rm T} \times P_{\rm soln} = 0.2665 \times 96.48 = 25.71 \text{ mm Hg}$ 

 $P_{\rm B} = x_{\rm B} \times P_{\rm soln} = 0.7335 \times 96.48 = 70.77 \text{ mm Hg}$ 

Ans. Total pressure :  $P_{\text{soln}} = 96.48 \text{ mm Hg}$ 

Partial pressures :  $P_{\text{Toluene}} = 25.71 \text{ mm Hg}$ 

 $P_{\text{Benzene}} = 70.77 \text{ mm Hg.}$ 

#### Additional Important Examples for Self-practice

- 1. Henry's law constant of methyl bromide (CH<sub>3</sub>Br), is 0.159 mol L<sup>-1</sup> bar<sup>-1</sup> at 25 °C. What is the solubility of methyl bromide in water at 25 °C and at pressure of 130 mm Hg? (Ans. S = 0.271 M)
- 2. The solubility of N<sub>2</sub> gas in water at 25 °C and 1 bar is  $6.85 \times 10^{-4}$  mol L<sup>-1</sup>. Calculate (a) Henry's law constant (b) molarity of N<sub>2</sub> gas dissolved in water under atmospheric conditions when partial pressure of N<sub>2</sub> in atmosphere is 0.75 bar.

(Ans. (a)  $K_{\rm H} = 6.85 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ bar}^{-1}$ 

(b) 
$$S = 5.138 \times 10^{-4} \text{ mol } \text{L}^{-1}$$
)

**3.** The vapour pressure of pure benzene (molar mass 78 g/mol) at a certain temperature is 640 mm Hg. A nonvolatile solute of mass 2.315 g is added to 49 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of solute?

(**Ans.** Molar mass =  $72.23 \text{ g mol}^{-1}$ )

- 4. The normal boiling point of ethyl acetate is 77.06 °C. A solution of 50 g of a nonvolatile solute in 150 g of ethyl acetate boils at 84.27 °C. Evaluate the molar mass of solute if  $K_b$  for ethyl acetate is 2.77 °C kg mol<sup>-1</sup>. (Ans. Molar mass = 128 g mol<sup>-1</sup>)
- 3.795 g of sulphur is dissolved in 100 g of carbon disulfide. This solution boils at 319.81 K. What is the molecular formula of sulphur in solution? The boiling point of the solvent is 319.45 K.
- (Ans. Molecular formula of sulphur = S<sub>8</sub>)
  6. 1.02 g of urea when dissolved in 98.5 g of certain solvent decreases its freezing point by 0.211 K. 1.609 g of unknown compound when dissolved in 86 g of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the unknown compound.

(Molar mass of urea =  $60 \text{ g mol}^{-1}$ ) (Ans. Molar mass =  $67.3 \text{ g mol}^{-1}$ )

- 7. What is the molar mass of a solute if a solution prepared by dissolving 0.822 g of it in 300 mdm<sup>3</sup> of water has an osmotic pressure of 149 mm Hg at 298 K?
  (Ans. Molar mass = 342 g mol<sup>-1</sup>)
- 8. The solubility of oxygen in water at 280 K and 500 mm Hg is  $0.01 \text{ g dm}^{-3}$ . Hence what is the solubility of O<sub>2</sub> at 750 mm Hg at same temperature? (Ans. 0.015 g dm<sup>-3</sup>)
- **9.** The vapour pressures of two liquids A and B are 80 mm and 60 mm respectively at 25 °C. What is the vapour pressure of the solution obtained by mixing 3 mol of A and 2 mol of B? (Ans. 72 mm Hg)
- 10. Calculate the osmotic pressure of 4.5 g of glucose (molar mass = 180) dissolved in 100 mL of water at 298 K.  $(R = 0.0821 \text{ L-atm mol}^{-1} \text{ K}^{-1})$  (Ans. 6.116 atm)
- **11.** A solution of cane sugar (molar mass =  $342 \text{ g mol}^{-1}$ ) containing 17.8 g L<sup>-1</sup> has an osmotic pressure 1.2 atm. Calculate the temperature of the solution. (R =  $0.082 \text{ L-atm mol}^{-1} \text{ K}^{-1}$ ) (Ans. 281.4 K)

### Chapter 3. Ionic Equilibria

(1) Dissociation constant of acetic acid is  $1.8 \times 10^{-5}$ . Calculate per cent dissociation of acetic acid in 0.01 M solution. (2 marks)

**Solution : Given :**  $K_a = 1.8 \times 10^{-5}$ ; C = 0.01 M

Per cent dissociation = ?

 $K_{a} = \frac{C\alpha^{2}}{1-\alpha} \approx C\alpha^{2}$   $\therefore \alpha = \sqrt{\frac{K_{a}}{C}} = \left(\frac{1.8 \times 10^{-5}}{0.01}\right)^{\frac{1}{2}} = 4.242 \times 10^{-2}$   $\therefore \text{ per cent dissociation} = \alpha \times 100$   $= 4.242 \times 10^{-2} \times 10^{2} = 4.242$ Ans. Per cent dissociation = 4.242.
(2) Calculate the pH of 0.01 M sulphuric acid. (2 marks) Solution : Given : C = 0.01 M H<sub>2</sub>SO<sub>4</sub>, pH = ? H<sub>2</sub>SO<sub>4(aq)</sub>  $\rightarrow 2H^{+}_{(aq)} + SO^{2-}_{4(aq)}$   $\therefore [H_{3}O^{+}] = 2 \times 0.01 = 0.02 \text{ M}$ pH =  $-\log_{10} [H_{3}O^{+}]$   $= -\log_{10} [H_{3}O^{+}]$   $= -\log_{10} 0.02$   $= -(\overline{2}.3010)$  = 2 - 0.3010 = 1.6990Ans. pH = 1.6990.

(3) The pH of a solution is 6.06. Calculate its  $[H_3O^+]$  ion concentration. (2 marks)

Solution : Given : pH = 6.06,  $[H_3O^+] = ?$   $pH = -\log_{10} [H_3O^+]$   $\therefore \log_{10} [H_3O^+] = -pH$   $\therefore [H_3O^+] = Antilog - pH$  = Antilog - 6.06  $= Antilog \overline{7}.94$   $= 8.714 \times 10^{-7} M$ Ans.  $[H_3O^+] = 8.714 \times 10^{-7} M$ .

(4) Calculate the pH of a buffer solution containing 0.1 M CH<sub>3</sub>COOH and 0.05 M CH<sub>3</sub>COONa. Dissociation constant of CH<sub>3</sub>COOH is  $1.8 \times 10^{-5}$  at 25 °C. (2 marks)

Solution : Given :  $[CH_3COOH] = 0.1 \text{ M},$   $[CH_3COONa] = 0.05 \text{ M}; K_a = 1.8 \times 10^{-5}; \text{ pH} = ?$   $pK_a = -\log_{10} K_a$   $= -\log_{10} 1.8 \times 10^{-5}$  $= -(\overline{5}.2553)$ 

$$= 5 - 0.2553$$
  
= 4.7447  
pH = pK<sub>a</sub> + log<sub>10</sub>  $\frac{[CH_3COONa]}{[CH_3COOH]}$   
= 4.7447 + log<sub>10</sub>  $\frac{0.05}{0.1}$   
= 4.7447 + ( $\overline{1}.6990$ )  
= 4.7447 + ( $-1 + 0.6990$ )  
= 4.7447 - 0.3010 = 4.4437  
**Ans.** pH = **4.4437.**

(5) Calculate the pH of buffer solution composed of 0.01 M weak base BOH and 0.02 M of its salt BA.  $[K_b = 1.8 \times 10^{-5}$  for weak base] (3 marks)

Solution : Given : [BOH] = 0.01 M;  
[BA] = 0.02 M; 
$$K_b = 1.8 \times 10^{-5}$$
; pH = ?  
 $pK_b = -\log_{10} K_b$   
 $= -\log_{10} 1.8 \times 10^{-5}$   
 $= -(\overline{5}.2553)$   
 $= 4.7447$   
pOH =  $pK_b + \log_{10} \frac{[Salt]}{[Base]}$   
 $= pK_b + \log_{10} \frac{[BA]}{[BOH]}$   
 $= 4.7447 + \log_{10} \frac{0.02}{0.01}$   
 $= 4.7447 + \log_{10} 2$   
 $= 4.7447 + 0.3010$   
 $= 5.0457$   
pH = 14 - pOH = 14 - 5.0457 = 8.9543  
Ans. pH = 8.9543.

(6) A buffer solution contains 0.3 M NH<sub>4</sub>OH and 0.4 M NH<sub>4</sub>Cl. If  $K_b$  for NH<sub>4</sub>OH is  $1.8 \times 10^{-5}$ , calculate pH of the solution. (3 marks) Solution : Given : [NH<sub>4</sub>OH] = 0.3 M; [NH<sub>4</sub>Cl] = 0.4 M;  $K_b = 1.8 \times 10^{-5}$ ; pH = ?

$$pK_{b} = -\log_{10} K_{b}$$

$$= -\log_{10} 1.8 \times 10^{-5}$$

$$= -(\overline{5}.2553)$$

$$= 4.7447$$

$$pOH = pK_{b} + \log_{10} \frac{[Salt]}{[Base]}$$

$$= 4.7447 + \log_{10} \frac{0.4}{0.3}$$

$$= 4.7447 + \log_{10} 1.333$$

$$= 4.7447 + 0.1248$$

$$= 4.8695$$

$$\therefore pH + pOH = 14$$

$$\therefore pH = 14 - pOH$$

$$= 14 - 4.8695 = 9.1305$$

Ans. pH = 9.1305.

(7) The solubility of AgBr in water is  $1.28 \times 10^{-5}$  mol/dm<sup>3</sup> at 298 K. Calculate the solubility product of AgBr at the same temperature.

(2 marks)

Solution : Given :  $S = 1.28 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $K_{sp} = ?$ AgBr dissociates as AgBr  $\Longrightarrow Ag^+_{(aq)} + Br^-_{(aq)}$ (solid)  $K_{sp} = [Ag^+][Br^-]$ As the solubility of AgBr in water is  $1.28 \times 10^{-5} \text{ mol/dm}^3$ ,  $[Ag^+] = [Br^-] = 1.28 \times 10^{-5} \text{ mol/dm}^3$   $\therefore K_{sp} = [1.28 \times 10^{-5}] [1.28 \times 10^{-5}] = 1.638 \times 10^{-10}$ Ans. Solubility product of AgBr =  $1.638 \times 10^{-10}$ .

## Additional Important Examples for Self-practice

1. Calculate pH and pOH of 0.01 M HCl solution.

(**Ans.** pH = 2; pOH = 12)

**2.** pH of solution is 3.12. Calculate the concentration of  $H_2O^+$  ion.

(Ans.  $[H_3O^+] = 7.586 \times 10^{-4} M$ )

**3.** A weak monobasic acid is 0.05% dissociated in 0.02 M solution. Calculate dissociation constant of the acid. (Ans.  $K_a = 5 \times 10^{-9}$ )

- 4. The dissociation constant of NH<sub>4</sub>OH is  $1.8 \times 10^{-5}$ . Calculate its degree of dissociation in 0.01 M solution. (Ans.  $\alpha = 0.04242$ )
- 5. A weak monobasic acid is 0.04% dissociated in 0.025 M solution. What is pH of the solution? (Ans. pH = 5)
- **6.** The pH of monoacidic weak base is 11.2. Calculate its per cent dissociation in 0.02 M solution. (**Ans.** Per cent dissociation = 7.925)
- 7. Calculate the pH of buffer solution composed of 0.1 M weak base BOH and 0.2 M of its salt BA.  $[K_b = 1.8 \times 10^{-5}$  for the weak base] (Ans. pH = 13.95)

8. The solubility product of AgBr is  $5.2 \times 10^{-13}$ . Calculate its solubility in mol dm<sup>-3</sup> and g dm<sup>-3</sup> (Molar mass of AgBr = 187.8 g mol<sup>-1</sup>) (Ans.  $S = 1.35 \times 10^{-4}$  g dm<sup>-3</sup>)

- 9. If 20.0 cm<sup>3</sup> of 0.050 M Ba(NO<sub>3</sub>)<sub>2</sub> are mixed with 20.0 cm<sup>3</sup> of 0.020 M NaF, will BaF<sub>2</sub> precipitate?  $K_{sp}$  of BaF<sub>2</sub> is  $1.7 \times 10^{-6}$  at 298 K. (Ans. Since IP >  $K_{sp}$ , BaF<sub>2</sub> will precipitate.)
- 10. Calculate the pH of buffer solution composed of 0.1 M weak base BOH and 0.2 M of its salt BA.  $[K_b = 1.8 \times 10^{-5} \text{ for the weak base}]$ (Ans. pH = 13.95)

#### **Chapter 4. Chemical Thermodynamics**

(1) Calculate the maximum work when 24 g of  $O_2$  are expanded isothermally and reversibly from the pressure of 1.6 bar to 1.0 bar at 298 K. (2 marks)

Solution : Given : 
$$W_{o2} = 24$$
 g,  $P_1 = 1.6$  bar,  $P_2 = 1$  bar,  
 $T = 298$  K,  $W_{max} = ?$   
 $W_{max} = -2.303 \ nRT \log_{10} \frac{P_1}{P_2}$   
 $= -2.303 \times \frac{W_{o2}}{M_{o2}} \times 8.314 \times 8.314 \times 298 \times \log_{10} \frac{1.6}{1}$   
 $= -2.303 \times \frac{24}{32} \times 8.314 \times 8.314 \times 298 \times 0.2041$   
 $= -873.4$  J  
Ans.  $W_{max} = -873.4$  J.

(2) Calculate  $\Delta U$  at 298 K for the reaction,  $C_2H_{4(g)} + HCl_{(g)} \rightarrow C_2H_5Cl_{(g)}, \Delta H = -72.3 \text{ kJ}.$ How much PV work is done? (3 marks) **Solution : Given :**  $C_2H_{4(g)} + HCl_{(g)} \rightarrow C_2H_5Cl_{(g)}$ T = 298 K;  $\Delta H = -72.3$  kJ; PV = ?;  $\Delta U = ?$  $\Delta n = \Sigma n_{2\text{gaseous products}} - \Sigma n_{1\text{gaseous reactants}}$ = 1 - (1 + 1) = -1 mol For PV work .  $W = -\Lambda nRT$  $= -(-1) \times 8.314 \times 298$ = 2478 I = 2.478 kI  $\Delta H = \Delta U + \Delta n R T$  $\Lambda U = \Lambda H - \Lambda nRT$ = -72.3 - (-2.478)= -69.82 kJ**Ans.** *PV* work = 2.478 kJ

 $\Delta U = -69.82 \text{ kJ.}$ 

(3) Calculate the work done during synthesis of  $NH_3$  in which volume changes from 8.0 dm<sup>3</sup> to 4.0 dm<sup>3</sup> at a constant external pressure of 43 bar. In what direction the work energy flows? (2 marks)

Solution : Given :  $V_1 = 8.0 \text{ dm}^3$ ;  $V_2 = 4.0 \text{ dm}^3$ ;  $P_{ex} = 43 \text{ bar}$ ; W = ?, What direction work energy flows?  $W = -P_{ex} (V_2 - V_1)$  = -43(4 - 8)  $= 172 \text{ dm}^3 \text{ bar}$   $= 172 \times 100 \text{ J}$  = 17200 J= 17.2 kJ.

In this compression process, the work is done on the system and work energy flows into the system.

(4) In a particular reaction, 2 kJ of heat is released by the system and 6 kJ of work is done on the system. Calculate  $\Delta U$ . (1 mark) Solution : Given : Q = -2 kJ; W = +6 kJ;  $\Delta U = ?$   $\Delta U = Q + W = -2 + (+6) = +4 \text{ kJ}$ Ans.  $\Delta U = +4 \text{ kJ}$ .

(5) The enthalpy change for the reaction,

 $C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$  is -620 J when 100 mL of ethylene and 100 mL of H<sub>2</sub> react at 1 bar pressure. Calculate the pressure volume type of work and  $\Delta U$  for the reaction. (3 marks)

Solution : Given : 
$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$
  
100 mL 100 ml 100 ml  
 $\Delta H = -620 \text{ J}; V_{C_2H_4} = 100 \text{ mL}; V_{H_2} = 100 \text{ mL}$   
 $P_{ex} = 1 \text{ bar}; W = ?; \Delta U = ?$   
 $\Delta V = 100 - (100 + 100) = -100 \text{ mL} = -0.1 \text{ dm}^3$   
 $W = -P_{ex} (V_2 - V_1)$   
 $= -P_{ex} \times \Delta V$   
 $= -1 \times (-0.1)$   
 $= 0.1 \text{ dm}^3 \text{ bar}$   
 $= 0.1 \times 100 \text{ J}$   
 $= +10 \text{ J}$   
 $\Delta H = \Delta U + P\Delta V$   
 $\therefore \Delta U = \Delta H - P\Delta V = -620 - (+10) = -610 \text{ J}$   
Ans.  $W = +10 \text{ J}; \Delta U = -610 \text{ J}.$ 

(6) Heat of evaporation of ethyl alcohol at  $78.5 \,^{\circ}\text{C}$  and 1 atmosphere is  $38.6 \,\text{kJ}\,\text{mol}^{-1}$ . If 100 g ethyl alcohol vapour is condensed, what will be  $\Delta H$ ? (2 marks)

Solution : Given :  $\Delta_{vap}H_{C_2H_5OH} = 38.6 \text{ kJ mol}^{-1}$ Mass of  $C_2H_5OH = m = 100 \text{ g}$ Molar mass of  $C_2H_5OH = M = 46 \text{ g mol}^{-1}$   $\Delta_{cond}H_{C_2H_5OH} = ?$ Number of moles of  $C_2H_5OH = \frac{m}{M} = \frac{100}{46} = 2.174 \text{ mol}$ Heat of condensation  $= \Delta_{cond}H = -38.6 \text{ kJ mol}^{-1}$   $\therefore \Delta_{cond}H = n \times \Delta_{cond}H$   $= 2.174_{mol} \times (-38.6)_{kJ mol}^{-1} \text{ kJ}$  = -83.9 kJAns. Heat of condensation  $= \Delta_{cond}H = -83.9 \text{ kJ}.$  (7) Calculate standard enthalpy of reaction,  $Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)},$ from the following data.  $\Delta_{\rm f} H^0_{\rm Fe,O_3} = -824 \text{ kJ/mol}, \ \Delta_{\rm f} H^0_{\rm CO} = -110 \text{ kJ/mol},$  $\Delta_{\rm f} H^0_{\rm CO_2} = -393$  kJ/mol. (3 marks) **Solution : Given :**  $\Delta_{\rm f} H^0_{\rm Fe,O_3} = -824 \text{ kJ/mol}$  $\Delta_{\rm f} H^0_{\rm CO} = -110 \text{ kJ mol}^{-1}$  $\Delta_{\rm f} H^0_{\rm CO_2} = -393 \text{ kJ/mol}; \Delta_{\rm r} H^0 = ?$ Required equation.  $\operatorname{Fe_2O_{3(s)}} + 3\operatorname{CO}_{(g)} \longrightarrow 2\operatorname{Fe}_{(s)} + 3\operatorname{CO}_{2(g)} \dots (I)$  $\Delta H_1 = ?$ Given equations :  $2Fe_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow Fe_2O_{3(s)}$ ... (II)  $C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)}$  $\dots$  (III)  $\times$  3  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$  $\dots$  (IV)  $\times$  3  $-2Fe_{(s)} \longrightarrow -Fe_2O_{3(s)} - 3CO_{(g)} + 3CO_{2(g)}$  $\therefore$  Fe<sub>2</sub>O<sub>3(s)</sub> + 3CO<sub>(g)</sub>  $\longrightarrow$  2Fe<sub>(s)</sub> + 3CO<sub>2(g)</sub> ... (I) Ea. (I) = - ea. (II) -3 eq. (III) +3 eq. (IV)  $\therefore \Delta H_1^0 = -\Delta H_2^0 - 3\Delta H_3^0 + 3\Delta H_4^0$ = -(-824) - 3(-110) + 3(-393)= 824 + 330 - 1179 $\therefore \Delta_r H^0 = -25 \text{ kJ}$ Ans.  $\Delta_r H^0 = -25$  kJ. (8) Calculate the standard enthalpy of formation of  $CH_3OH_{(l)}$ 

from the following data :

- (i)  $CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}, \Delta H^0 = -726 \text{ kJ mol}^{-1}$
- (ii) C(Graphite) +  $O_{2(g)} \longrightarrow CO_{2(g)}, \Delta_c H^0 = -393 \text{ kJ mol}^{-1}$

(iii) 
$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2 O_{(l)}, \Delta_f H^0 = -286 \text{ kJ mol}^{-1}$$
 (3 marks)

Solution : Given : 
$$\Delta_{c}H^{0}_{CH_{3}OH} = -726 \text{ kJ mol}^{-1}$$
;  
 $\Delta_{f}H^{0}_{CO_{2}} = -393 \text{ kJ mol}^{-1}$ ;  
 $\Delta_{f}H^{0}_{H_{2}O} = -286 \text{ kJ mol}^{-1}$ ;  
 $\Delta_{f}H^{0}_{CH_{3}OH} = ?$ 

Required thermochemical equation :

$$C_{(s)} + 2H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CH_3OH_{(l)}$$
 ... (I)  $\Delta H_1^0 = ?$ 

Given equations :

$$\overline{C}H_{3}OH_{(l)} = \frac{3}{2} O_{2(g)} \longrightarrow \overline{2} CO_{2(g)} + 2H_{2}O_{(l)} \dots (II) \Delta H_{2}^{0}$$

$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \dots (III) \Delta H_{3}^{0}$$

$$+$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_{2}O_{(l)} \dots (IV) \Delta H_{4}^{0} \times 2$$

$$+$$
Eq. (I) = - eq. (II) + eq. (III) + 2 eq. (IV)
$$\therefore \Delta H_{1}^{0} = -\Delta H_{2}^{0} + \Delta H_{3}^{0} + 2\Delta H_{4}^{0}$$

$$= -(-726) + (-393) + 2(-286)$$

$$= 726 - 393 - 572$$

$$= -239 \text{ kJ mol}^{-1}$$

Ans. Standard enthalpy of formation =  $\Delta_f H^0 = -239 \text{ kJ mol}^{-1}$ .

(9) Calculate the standard enthalpy of formation of  $\rm CH_3OH_{(l)}$  from the following data :

(i) 
$$CH_{3}OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_{2}O_{(l)}, \Delta H^{0} = -726 \text{ kJ mol}^{-1}$$
  
(ii)  $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}, \Delta_{c}H^{0} = -393 \text{ kJ mol}^{-1}$   
(iii)  $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_{2}O_{(l)}, \Delta_{f}H^{0} = -286 \text{ kJ mol}^{-1}$  (3 marks)  
Solution : Required equation :  
 $C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CH_{3}OH_{(l)}$  ... (I)  $\Delta H_{I} = ?$ 

Reverse equation (1), multiply equation (3) by 2 and add these to equation (2)

$$\begin{split} \mathrm{CO}_{2(\mathrm{g})} + 2\mathrm{H}_{2}\mathrm{O}_{(l)} + \mathrm{C}_{(\mathrm{s})} + \mathrm{O}_{2(\mathrm{g})} + 2\mathrm{H}_{2(\mathrm{g})} + \mathrm{O}_{2(\mathrm{g})} &\longrightarrow \\ \mathrm{CH}_{3}\mathrm{OH}_{(l)} + \frac{3}{2} \, \mathrm{O}_{2(\mathrm{g})} + \mathrm{CO}_{2(\mathrm{g})} + 2\mathrm{H}_{2}\mathrm{O}_{(l)} \\ \therefore \ \Delta H_{\mathrm{f}}^{0} &= -\Delta H_{1}^{0} + \Delta H_{2}^{0} + 2\Delta H_{3}^{0} \\ &= -(-726) + (-393) + 2(-286) \\ &= -239 \text{ kJ mol}^{-1} \\ \mathbf{Ans.} \ \Delta_{\mathrm{f}} H_{\mathrm{CH}_{3}\mathrm{OH}}^{0} &= -\mathbf{239 \ kJ \ mol}^{-1}. \end{split}$$

(10) Calculate the standard enthalpy of formation of  $CH_3 - OH$ ,

if standard heat of combustion of methyl alcohol are -726 kJ mol<sup>-1</sup>.

Given data :

(i) 
$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}, \Delta H^0 = -726 \text{ kJ mol}^{-1}$$

- (ii)  $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}, \Delta_c H^0 = -393 \text{ kJ mol}^{-1}$
- (iii)  $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2 O_{(l)}, \Delta_f H^0 = -286 \text{ kJ mol}^{-1}.$  (3 marks)

Solution : Given equations :

$$CH_{3}OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_{2}O_{(l)} \qquad \dots (I) \Delta H_{1}$$
$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \dots (II) \Delta H_{2}$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2 O_{(l)} \qquad \qquad \dots \text{ (III) } \Delta H_3$$

Required equation :

$$C_{(\text{graphite})} + 2H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CH_3OH_{(1)} \qquad \dots \text{ (IV) } \Delta H_4 = ?$$
  
Now,  $\Delta H_4 = 2 \Delta H_3 + \Delta H_2 - \Delta H_1$   
 $= 2 \times (-286) + (-393) - (-726)$   
 $= -239 \text{ kJ mol}^{-1}$ 

Ans.  $\Delta_{\rm f} H_{\rm CH_2OH} = -239 \text{ kJ mol}^{-1}$ .

(11) Calculate the standard enthalpy of

$$\begin{split} & N_2 H_{4(g)} + H_{2(g)} \longrightarrow 2 N H_{3(g)} \\ & \text{if} \qquad \Delta H^0_{N-H} = 389 \text{ kJ mol}^{-1} \\ & \Delta H^0_{H-H} = 435 \text{ kJ mol}^{-1} \\ & \Delta H^0_{N-N} = 159 \text{ kJ mol}^{-1}. \end{split}$$
 (3 marks)

Solution: 
$$\frac{H}{H} > N - N < \frac{H}{H_{(g)}} + H - H_{(g)} \longrightarrow 2 N < \frac{H}{H}$$
  
Bond enthalpies:  $\Delta H^{0}_{(N-H)} = 389 \text{ kJ mol}^{-1}$ ;  
 $\Delta H^{0}_{(H-H)} = 435 \text{ kJ mol}^{-1}$ ;  $\Delta H^{0}_{(N-N)} = 159 \text{ kJ mol}^{-1}$ ;  $\Delta_{r}H^{0} = ?$   
 $\Delta_{r}H^{0} = \Sigma \Delta H^{0}_{(reactants)} - \Sigma \Delta H^{0}_{(products)}$   
 $= (4\Delta H^{0}_{N-H} + \Delta H^{0}_{N-N} + \Delta H^{0}_{H-H}) - 6(\Delta H^{0}_{N-H})$   
 $= (4 \times 389 + 159 + 435) - 6 \times 389$   
 $= (1556 + 159 + 435) - 2334$   
 $= -184 \text{ kJ}.$ 

Ans.  $\Delta_{\rm r} H^0 = -184 \text{ kJ}$ 

## Additional Important Examples for Self-practice

- 1. 2 moles of an ideal gas are expanded isothermally and reversibly from 20 L to 30 L at 300 K. Calculate the work done.  $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$  (Ans.  $W_{\text{max}} = -2023 \text{ J}$ )
- 2. 22 g of  $CO_2$  are compressed isothermally and reversibly at 298 K from initial pressure of 100 kPa when the work obtained is 1.2 kJ. Find the final pressure. (Ans. P = 263.4 kPa)
- 300 mmol of an ideal gas occupies 13.7 dm<sup>3</sup> at 300 K. Calculate the work done when the gas is expanded until its volume has increased by 2.3 dm<sup>3</sup> (a) isothermally against a constant external pressure of 0.3 bar (b) isothermally and reversibly (c) into vacuum.

(Ans. (a) W = -69 J; (b)  $W_{max} = -116.1$  J (c)  $W_{vacuum} = 0$ ) 4.  $\Delta H$  for the reaction,

2C<sub>(s)</sub> + 3H<sub>2(g)</sub> → C<sub>2</sub>H<sub>6(g)</sub> is -84.4 kJ at 25 °C. Calculate Δ*U* for the reaction at 25 °C. (*R* = 8.314 JK<sup>-1</sup> mol<sup>-1</sup>) (Ans. Δ*U* = -79.44 kJ) 5. Calculate standard enthalpy of reaction,

5. Currentiate standard entitipy of reaction,  $2C_2H_{6(g)} + 7O_{2(g)} \longrightarrow 4CO_{2(g)} + 6H_2O_{(l)}$ Given that  $\Delta_f H^0(CO_2) = -393.5 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^0(H_2O) = -285.8 \text{ kJ mol}^{-1}$  and  $\Delta_f H^0(C_2H_6) = -84.9 \text{ kJ mol}^{-1}$  (Ans.  $\Delta_r H^0 = -3119 \text{ kJ}$ ) 6. Estimate the standard enthalpy of combustion of  $CH_{4(g)}$  if  $\Delta_f H^0(CH_4) = -74.8 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^0(CH_4) = -202.5 \text{ kJ mol}^{-1}$ 

 $\Delta_{\rm f} {\it H}^0({\rm CO}_2) = -\,393.5~{\rm kJ}~{\rm mol}^{-1}$  and

 $\Delta_{\rm f} H^0({\rm H_2O}) = -285.8 \text{ kJ mol}^{-1}$  (Ans.  $\Delta_{\rm c} H^0_{({\rm CH_4})} = -890.3 \text{ kJ}$ )

- 7. The enthalpy change of the following reaction,  $CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_{3}Cl_{(g)} + HCl_{(g)}, \Delta_{r}H^{0} = -104 \text{ kJ}.$ Calculate C - Cl bond enthalpy. The bond enthalpies are Bond C - H Cl - Cl H - Cl  $\Delta H^{0}/\text{kJ mol}^{-1}$  414 243 431 (Ans.  $\Delta H^{0}_{Cl-Cl} = 330 \text{ kJ mol}^{-1}$ )
- 8. Calculate the standard enthalpy of the reaction,

$$2Fe_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow Fe_2O_{3(s)}$$

Given :

11.

(i)  $2Al_{(s)} + Fe_2O_{3(s)} \longrightarrow 2Fe_{(s)} + Al_2O_{3(s)}, \Delta_r H^0 = -847.6 \text{ kJ}$ (ii)  $2Al_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow Al_2O_{3(s)}, \Delta_r H^0 = -1670 \text{ kJ}$ 

9. Calculate the heat of reaction of the following reaction :  $CH_3COOH_{(l)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)} + 2H_2O_{(l)}$ Given that heat of formation of  $CO_{2(g)}$ ,  $H_2O_{(l)}$  and  $CH_3COOH_{(l)}$ are  $-395.50 \text{ kJ mol}^{-1}$ ,  $-285.77 \text{ kJ mol}^{-1}$  and  $-490.85 \text{ kJ mol}^{-1}$ respectively. (Ans.  $-871.69 \text{ kJ mol}^{-1}$ )

(Ans.  $\Delta_r H^0 = -822.4 \text{ kJ}$ )

**10.** Calculate the standard enthalpy of formation of benzene from the following data :

$$C_{6}H_{6(1)} + \frac{15}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_{2}O_{(l)}; \quad \Delta H^{0} = -3267 \text{ kJ}$$

$$\Delta_{f}H^{0}_{(CO_{2})} = -393.5 \text{ kJ mol}^{-1};$$

$$\Delta_{f}H^{0}_{(H_{2}O)} = -285.8 \text{ kJ mol}^{-1} \qquad (\text{Ans. } \Delta_{f}H^{0}_{C_{6}H_{6}} = 48.6 \text{ kJ mol}^{-1})$$
Calculate the standard enthalpy of the reaction,  

$$SiO_{2(s)} + 3C_{(graphite)} \longrightarrow SiC_{(s)} + 2CO_{(g)}$$
from the following reactions,  
(i)  $Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}, \qquad \Delta_{r}H^{0} = -911 \text{ kJ}$   
(ii)  $2C_{(graphite)} + O_{2(g)} \longrightarrow 2CO_{(g)}, \qquad \Delta_{r}H^{0} = -221 \text{ kJ}$ 

(iii) 
$$\operatorname{Si}_{(s)} + \operatorname{C}_{(\text{graphite})} \longrightarrow \operatorname{SiC}_{(s)}, \qquad \Delta_{\mathrm{r}} H^0 = -65.3 \text{ kJ}$$
  
(Ans.  $\Delta_{\mathrm{r}} H^0 = +624 \text{ kJ}$ )

#### Chapter 5. Electrochemistry

(1) The conductivity of 0.02 M AgNO<sub>3</sub> at 25 °C is  $2.428 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ . What is its molar conductivity? (2 marks) **Solution : Given :** Concentration of solution = C = 0.02 M AgNO<sub>3</sub> Temperature = T = 273 + 25 = 298 KConductivity =  $\kappa = 2.428 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$  (or S cm<sup>-1</sup>) Molar conductivity =  $\wedge_m = ?$  $\wedge_{\rm m} = \frac{\kappa \times 1000}{C} = \frac{2.428 \times 10^{-3} \times 1000}{0.02}$ = 121.4  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (or 121.4 S cm<sup>2</sup> mol<sup>-1</sup>) Ans. Molar conductivity =  $\wedge_m = 121.4 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ . (2) 0.05 M NaOH solution offered a resistance of 31.6  $\Omega$  in a conductivity cell at 298 K. If the cell constant of the cell is  $0.367 \text{ cm}^{-1}$ , calculate the molar conductivity of NaOH solution. (3 marks) **Solution : Given :** Concentration = C = 0.05 M NaOH Resistance =  $R = 31.6 \Omega$ Cell constant = b = 0.367 cm<sup>-1</sup>  $\wedge_{m (NaOH)} = ?$ 

$$\kappa_{\text{(NaOH)}} = \frac{b}{R_{\text{NaOH}}} = \frac{0.367}{31.6} = 0.01161 \ \Omega^{-1} \text{ cm}^{-1}$$

$$\wedge_{\rm m(NaOH)} = \frac{\kappa \times 1000}{\rm C}$$

$$= \frac{0.01161 \times 1000}{0.05}$$
$$= 232.2 \ \Omega^{-1} \ \mathrm{cm}^2 \ \mathrm{mol}^{-1}$$

Ans. Molar conductivity =  $\wedge_m = 232.1 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ .

(3) The molar conductivity of 0.01 M acetic acid at 25 °C is 18  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Calculate its degree of dissociation in 0.01 M solution and dissociation constant, if molar conductivity of acetic acid at zero concentration is 400  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. (2 marks)

Solution : Given :

C = 0.01 M; 
$$\wedge_{\rm m} = 18 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1};$$
  
 $\wedge_0 = 400 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}; \ \alpha = ?; \ K_{\rm a} = ?$   
 $\alpha = \frac{\Lambda_{\rm m}}{\Lambda_0} = \frac{18 \ {\rm cm}^2 \ {\rm mol}^{-1}}{400 \ {\rm cm}^2 \ {\rm mol}^{-1}} = 0.045$ 

$$K_{a} = \frac{C\alpha^{2}}{1-\alpha}$$
$$= \frac{0.01 \times (0.045)^{2}}{1-0.045}$$
$$= 2.12 \times 10^{-5}$$

Ans.  $\alpha = 0.045$ ;  $K_a = 2.12 \times 10^{-5}$ .

(4) The molar conductivities at zero concentration (or at infinite dilution) of CH<sub>3</sub>COONa, HCl and NaCl in  $\Omega^{-1}$ cm<sup>2</sup>mol<sup>-1</sup> are 90.8, 426.2 and 126.4 respectively. Calculate the molar conductivity of CH<sub>3</sub>COOH at infinite dilution. (2 marks)

**Solution : Given :** 
$$\wedge_{0(CH_3COONa)} = 90.8 \ \Omega^{-1} cm^2 mol^{-1}$$

$$\wedge_{0(\text{HCl})} = 426.2 \ \Omega^{-1} \text{cm}^2 \,\text{mol}^{-1}$$

 $\wedge_{0(\text{NaCl})} = 126.4 \ \Omega^{-1} \text{cm}^2 \text{ mol}^{-1}$ 

 $\wedge_{0(CH_3COOH)} = ?$ 

By Kohlrausch's law

$$\wedge_{0(CH_{3}COOH)} = \lambda_{CH_{3}COO^{-}}^{0} + \lambda_{H^{+}}^{0} \qquad ... (I)$$

$$\wedge_{0(\mathrm{CH}_{3}\mathrm{COONa})} = \lambda_{0\mathrm{CH}_{3}\mathrm{COO}^{-}} + \lambda_{\mathrm{Na}^{+}}^{0} \qquad \dots (i)$$

$$\wedge_{0(\text{HCl})} = \lambda_{\text{H}^{+}}^{0} + \lambda_{\text{Cl}^{-}}^{0} \qquad \dots \quad (\text{ii})$$

$$\wedge_{0(\text{NaCl})} = \lambda_{\text{Na}^{+}}^{0} + \lambda_{\text{Cl}^{-}}^{0} \qquad \dots (iii)$$

Adding equations (i) and (ii) and subtracting equation (iii) we get equation (I).

$$\therefore \wedge_{0(CH_{3}COOH)} = \wedge_{0CH_{3}COONa} + \wedge_{0HCl} - \wedge_{0NaCl} \qquad \dots (I)$$
  
= 90.8 + 426.2 - 126.4  
= 390.6  $\Omega^{-1} cm^{2} mol^{-1}$ 

Ans.  $\wedge_{0(CH_{3}COOH)} = 390.6 \ \Omega^{-1} cm^{2} mol^{-1}$ .

(5) The molar conductivities at zero concentrations of NH<sub>4</sub>Cl, NaOH and NaCl are respectively 149.7  $\Omega^{-1}$ cm<sup>2</sup> mol<sup>-1</sup>, 248.1  $\Omega^{-1}$ cm<sup>2</sup> mol<sup>-1</sup> and 126.5  $\Omega^{-1}$ cm<sup>2</sup> mol<sup>-1</sup>. What is the molar conductivity of NH<sub>4</sub>OH at zero concentration? (2 marks)

**Solution : Given :** 
$$\wedge_{0(\text{NH}_{4}\text{Cl})} = 149.7 \ \Omega^{-1}\text{cm}^{2} \text{ mol}^{-1}$$
  
 $\wedge_{0(\text{NaOH})} = 248.1 \ \Omega^{-1}\text{cm}^{2} \text{ mol}^{-1}$   
 $\wedge_{0(\text{NaCl})} = 126.5 \ \Omega^{-1}\text{cm}^{2} \text{ mol}^{-1}$   
 $\wedge_{0(\text{NH}_{4}\text{OH})} = ?$ 

By Kohlrausch's law

$$\wedge_{0(\mathrm{NH}_{4}\mathrm{OH})} = \lambda_{\mathrm{NH}_{4}^{+}}^{0} + \lambda_{\mathrm{OH}^{-}}^{0} \qquad \dots \qquad I$$

$$\wedge_{0(\mathrm{NH}_{4}\mathrm{CI})} = \lambda_{\mathrm{NH}_{4}} + \lambda_{\mathrm{CI}} - \dots \quad (1)$$

$$\Lambda_{0(\text{NaOH})} = \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-} \qquad \dots \qquad (11)$$

$$\wedge_{0(\text{NaCl})} = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} \qquad \dots \quad (\text{iii})$$

Adding equations (i) and (ii) and subtracting equation (iii) we get equation (I).

$$\therefore \ \wedge_{0(\text{NH}_{4}\text{OH})} = \wedge_{0(\text{NH}_{4}\text{CI})} + \wedge_{0(\text{NaOH})} - \wedge_{0(\text{NaCI})} \qquad \dots \ \text{I}$$
$$= 149.7 + 248.1 - 126.5$$
$$= 271.3 \ \Omega^{-1} \text{cm}^{2} \text{mol}^{-1}$$

Ans.  $\wedge_{0(NH_4OH)} = 271.3 \ \Omega^{-1} \text{cm}^2 \text{ mol}^{-1}$ .

(6) How many electrons would have a total charge of 1 coulomb?

(2 marks)

Solution : Given : 1 Faraday  $\equiv$  charge on 1 mol of electrons = 6.022 × 10<sup>23</sup> electrons and 1 Faraday = 96500 C  $\therefore$  96500 C  $\equiv$  6.022 × 10<sup>23</sup> electrons  $\therefore$  1 C  $\equiv \frac{6.022 \times 10^{23}}{96500} = 6.24 \times 10^{18}$  electrons

Ans. Number of electrons =  $6.24 \times 10^{18}$ .

(7) How many moles of electrons are required for reduction of 2 moles of  $Zn^{2+}$  to Zn? How many Faradays of electricity will be required? (2 marks)

Solution : Given : Moles of  $Zn^{2+} = 2$ ; Number of Faradays required = ?  $Zn_{(aq)}^{2+} + 2e^{-} \longrightarrow Zn_{(s)}$ 1 mol 2 mol = 2 Faradays  $\therefore$  1 mol  $Zn^{2+}$  require 2 Faradays  $\therefore$  2 mol  $Zn^{2+}$  will require 4 Faradays Ans. 4 Faradays of electricity. (8) What is standard cell potential for the reaction  $3Ni_{(s)} + 2Al^{3+}$  (1 M)  $\longrightarrow$   $3Ni^{2+}$  (1 M)  $+ 2Al_{(s)}$ if  $E_{Ni}^{0} = -0.25$  V and  $E_{Al}^{0} = -1.66$  V? (2 marks)

**Solution : Given :**  $E_{Ni^{2+}/Ni}^0 = -0.25$  V;  $E_{\Delta 1^{3+}/\Delta 1}^{0} = -1.66 \text{ V}; E_{cell}^{0} = ?$ Since Ni is oxidised and  $A1^{3+}$  is reduced  $E_{\text{cell}}^{0} = E_{\text{Al}^{3+}/\text{Al}}^{0} - E_{\text{Ni}^{2+}/\text{Ni}}^{0}$ = -1.66 - (-0.25)= -1.41 VAns.  $E_{cell}^0 = -1.41$  V. (9) Construct a galvanic cell from the electrodes Co<sup>3+</sup>|Co and  $Mn^{2+}|Mn. E_{Co}^{0} = 1.82 V, E_{Mn}^{0} = -1.18 V.$  Calculate  $E_{cell}^{0}$ . (2 marks) **Solution : Given :**  $E_{Co^{3+}|Co}^0 = 1.82$  V;  $E_{Mn^{2+}|Mn}^0 = -1.18$  V;  $E_{cell}^{0} = ?$ The galvanic cell is,  $Mn_{(s)} | M^{2+} (1 M) || Co^{3+} (1 M) | Co_{(s)}$  $E_{\text{cell}}^{0} = E_{\text{Co}^{3+}|\text{Co}}^{0} - E_{\text{Mn}^{2+}|\text{Mn}}^{0}$ = 1.82 - (-1.18)= 30 V**Ans.**  $E_{cell}^0 = 3.0$  V. (10) Calculate  $E_{cell}^0$  and  $\Delta G^0$  for the reaction  $2Cu^+ \longrightarrow Cu^{2+} + Cu$ .  $E_{\text{Cu}^+|\text{Cu}}^0 = 0.52 \text{ V}$  and  $E_{\text{Cu}^{+2},\text{Cu}^+}^0 = 0.16 \text{ V}.$ (3 marks) **Solution : Given :** Cell reaction :  $2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu^{(s)}_{(s)}$  $E_{Cu^+|Cu}^0 = 0.52 \text{ V}; E_{Cu^{2+}|Cu^+}^0 = 0.16 \text{ V}$ 1F = 96500 C $E_{\text{cell}}^{0} = ?; \quad \Delta G^{0} = ?$ (i) The formulation of the cell : Pt | Cu<sup>+</sup><sub>(aq)</sub>, cu<sup>2+</sup><sub>(aq)</sub> || Cu<sup>+</sup><sub>(aq)</sub> | Cu<sup>(s)</sup> LHE  $Cu_{(aq)}^+ \longrightarrow Cu_{(aq)}^{2+} + e^-$ (Oxidation at anode) RHE  $Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)}$ (Reduction at cathode)  $2Cu^+_{(2q)} \longrightarrow Cu^{2+}_{(2q)} + Cu_{(q)}$ (Overall cell reaction) :. n = 1 $E_{\text{cell}}^{0} = E_{\text{Cu}^{+}|\text{Cu}}^{0} - E_{\text{Cu}^{2+}|\text{Cu}^{+}}^{0}$ (cathode) (anode) = 0.52 - 0.16 = 0.36 V

(ii) 
$$\Delta G^0 = -nFE^0_{cell} = -1 \times 96500 \times 0.36 = -34740 \text{ J}$$
  
= -34.74 kJ

**Ans.** (i)  $E_{\text{cell}}^0 = 0.36 \text{ V}$  (ii)  $\Delta G^0 = -34.74 \text{ kJ}$ .

### Additional Important Examples for Self-practice

1. The molar conductivity of 0.05 M BaCl<sub>2</sub> solution at 25 °C is 223  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. What is its conductivity?

(Ans.  $\kappa = 0.01115 \Omega^{-1} \text{ cm}^{-1}$ )

2. Calculate the molar conductivity of AgI at zero concentration if the molar conductivities of NaI, AgNO<sub>3</sub> and NaNO<sub>3</sub> at zero concentration are respectively, 126.9, 133.4 and 121.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

(Ans.  $\wedge_{0(AgI)} = 138.8 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ )

**3.** A conductivity cell containing 0.01 M KCl gives at 25 °C the resistance of 604 ohms. The same cell containing 0.001 M AgNO<sub>3</sub> gives resistance of 6530 ohms. Calculate the molar conductivity of 0.001 M AgNO<sub>3</sub>.

[Conductivity of 0.01 M KCl at 25 °C is 0.00141  $\Omega^{-1}$  cm<sup>-1</sup>] (Ans.  $\wedge_{m(AgNO_3)} = 130 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ )

- 4. What is the mass of Cu metal produced at the cathode during the passage of 5 ampere current, through  $CuSO_4$  solution for 100 minutes. Molar mass of Cu is 63.5 g mol<sup>-1</sup>. (Ans.  $W_{Cu} = 9.87$  g)
- 5. The molar conductivity of 0.01 M acetic acid at 25 °C is 16.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Calculate its degree of dissociation in 0.01 M solution and dissociation constant if molar conductivity of acetic acid at zero concentration is 390.7  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

(Ans.  $\alpha = 0.0422$ ;  $K_a = 1.85 \times 10^{-5}$ )

- 6. How long will it take to produce 2.415 g of Ag metal from its salt solution by passing a current of 3 ampere? Molar mass of Ag is  $107.9 \text{ g mol}^{-1}$ . (Ans. t = 12 min)
- 7. How many moles of electrons are required for reduction of 3 moles of Zn<sup>2+</sup> to Zn? How many Faradays of electricity will be required? (Ans. 6 mol electrons, 6 Faradays)

8. Calculate the voltage of the cell,  $Sn_{(s)} | Sn^{2+} (0.02 \text{ M}) || Ag^{+} (0.01 \text{ M}) | Ag_{(s)} \text{ at } 25 \text{ °C.}$   $E^{0}_{Sn} = -0.136 \text{ V}, E^{0}_{Ag} = 0.800 \text{ V.}$  (Ans.  $E_{cell} = 0.8679 \text{ V}$ ) 9. The standard potential of the electrode,  $Zn^{2+} (0.02 \text{ M}) | Zn_{(s)} \text{ is } -0.76 \text{ V.}$  Calculate its potential. (Ans.  $E_{Zn^{++}|Zn} = -0.81 \text{ V}$ ) 10. Calculate the voltage of the cell,  $Sn_{(s)} | Sn^{2+}(0.02 \text{ M}) || Ag^{+} (0.01 \text{ M}) | Ag_{(s)} \text{ at } 25 \text{ °C.}$ 

 $E_{\rm Sn}^0 = -0.136 \text{ V}, E_{\rm Ag}^0 = 0.800 \text{ V}.$  (Ans.  $E_{\rm cell} = 0.8679 \text{ V}$ )

#### **Chapter 6. Chemical Kinetics**

(1) The rate of decomposition of  $N_2O_5$  was studied in liquid bromine,  $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$ .

If at a certain time, the rate of disappearance of  $N_2O_5$  is 0.015 M s<sup>-1</sup> find the rates of formation of NO<sub>2</sub> and O<sub>2</sub>. What is the rate of the reaction at this instant? (3 marks)

Solution : Given :  $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$ Rate of disappearance of  $N_2O_5 = 0.015$  M s<sup>-1</sup>

Rate of formation of  $NO_2 = ?$ 

Rate of formation of  $O_2 = ?$ 

Rate of reaction = ?

Rate of disappearance of N<sub>2</sub>O<sub>5</sub> =  $\frac{-d[N_2O_5]}{dt}$  = 0.015 M s<sup>-1</sup>

Since 4 moles of  $NO_2$  are formed from 2 moles of  $N_2O_5$ ,

Rate of formation of  $NO_2 = 2 \times Rate$  of disappearance of  $N_2O_5$ 

$$= 2 \times \frac{(-d [N_2 O_5])}{dt}$$

$$\therefore \frac{d[\text{NO}_2]}{dt} = 2 \times 0.015 = 0.03 \text{ M} \text{ s}^{-1}$$

Rate of formation of  $O_2 = \frac{1}{2}$  Rate of disappearance of  $N_2O_5$ =  $\frac{1}{2} \left( \frac{-d[N_2O_5]}{2} \right)$ 

$$=\frac{1}{2} \times 0.015 = 0.0075 \text{ M} \text{ s}^{-1}$$

Rate of reaction =  $R = \frac{1}{2} \left( \frac{-d [N_2 O_5]}{dt} \right)$ =  $\frac{1}{2} \times 0.015 = 0.0075 \text{ M s}^{-1}$ =  $\frac{1}{4} \left( \frac{d [NO_2]}{dt} \right) = \frac{1}{4} \times 0.03 = 0.0075 \text{ M s}^{-1}$ =  $\frac{d [O_2]}{dt} = 0.0075 \text{ M s}^{-1}$ 

Ans. Rate of formation of NO<sub>2</sub> = 0.03 M s<sup>-1</sup> Rate of formation of O<sub>2</sub> = 0.0075 M s<sup>-1</sup> Rate of reaction = 0.0075 M s<sup>-1</sup>.

(2) The reaction  $F_{2(g)} + 2ClO_{2(g)} \longrightarrow 2FClO_{2(g)}$  is first order in each of the reactant. The rate of the reaction is  $4.88 \times 10^{-4}$  M/s when  $[F_2] = 0.015$  M and  $[ClO_2] = 0.025$  M. Calculate the rate constant of the reaction. (3 marks)

Solution : Given :  $F_{2(g)} + 2CIO_{2(g)} \longrightarrow 2FCIO_{2(g)}$ Order of reaction in  $F_2 = n_{F_2} = 1$ Order of reaction in  $CIO_2 = n_{CIO_2} = 1$ Rate  $= R = 4.88 \times 10^{-4} \text{ M s}^{-1}$   $[F_2] = 0.015 \text{ M}; [CIO_2] = 0.025 \text{ M}$ Rate constant = k = ?By rate law Rate  $= R = k [F_2] [CIO_2]$  $\therefore k = \frac{R}{[F_2] [CIO_2]} = \frac{4.88 \times 10^{-4} \text{ M s}^{-1}}{0.015 \text{ M} \times 0.025 \text{ M}} = 1.3 \text{ M}^{-1} \text{s}^{-1}$ 

**Ans.** Rate constant =  $k = 1.3 \text{ M}^{-1} \text{s}^{-1}$ .

(3) Determine the order of following reactions from their rate expressions :

(a) 
$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
 Rate =  $k[H_2O_2]$   
(b)  $NO_2 + CO \longrightarrow NO + CO_2$  Rate =  $k[NO_2]^2$   
(c)  $2NO + O_2 \longrightarrow 2NO_2$  Rate =  $k[NO]^2 \times [O_2]$  (3 marks)

## Solution :

(a) For the reaction

 $2H_2O_2 \longrightarrow 2H_2O + O_2$ Since the rate law expression given is Rate =  $k[H_2O_2]$ The reaction is of first order.

(b) For the reaction

 $NO_2 + CO \longrightarrow NO + CO_2$ ,

since the rate law given is

Rate =  $k[NO_2]^2$ , the reaction is second order with respect to NO<sub>2</sub> and zero order with respect to CO. Hence the net order of the reaction is

 $n = n_{\rm NO_2} + n_{\rm CO} = 2 + 0 = 2$ 

(c) For the reaction

 $2NO + O_2 \longrightarrow 2NO_2$ ,

since the rate law expression given is

Rate =  $k[NO]^2 \times [O_2]$  the reaction is second order with respect to NO and first order with respect to O<sub>2</sub>. Hence the overall order of reaction is

 $n = n_{\rm NO_2} + n_{\rm O_2} = 2 + 1 = 3.$ 

(4) For the reaction,  $CH_3Br_{(aq)} + OH_{(aq)}^- \longrightarrow CH_3OH + Br_{(aq)}^-$ , rate law is, rate =  $k[CH_3Br][OH^-]$ .

- (a) How does reaction rate change if [OH<sup>-</sup>] is decreased by a factor of 5?
- (b) What is the change in rate if concentrations of both reactants are doubled? (2 marks)

Solution : Given :

(a) Rate = 
$$R = k[CH_3Br] \times [OH^-]$$
  
If  $R_1$  and  $R_2$  are initial and final rates of reaction then  
 $R_1 = k[CH_3Br] \times [OH^-]_1$   
 $R_2 = k[CH_3Br] \times [OH^-]_2$   
 $= k[CH_3Br] \times \frac{1}{5} \times [OH^-]_1$ 

$$\therefore \frac{R_2}{R_1} = \frac{k [CH_3Br] \times \frac{1}{5} \times [OH^-]_1}{k [CH_3Br] \times [OH^-]_1} = \frac{1}{5}$$
  
$$\therefore R_2 = \frac{1}{5} \times R_1$$
  
(b)  $R_1 = k \times [CH_3Br] \times [OH^-]$   
 $R_2 = k \times 2 \times [CH_3Br] \times 2 \times [OH^-]$   
$$\therefore \frac{R_2}{R_1} = \frac{k \times 2 \times [CH_3Br] \times 2 \times [OH^-]}{k \times [CH_3Br] \times [OH^-]} = 4$$
  
$$\therefore R_2 = 4R_1$$
  
Rate will be increased 4 time.

#### Ans. (a) Rate of the reaction decreases five times.

- (b) Rate of the reaction increases four times.
- (5) A reaction takes place in two steps,

(i) 
$$NO_{(g)} + Cl_{2(g)} \longrightarrow NOCl_{2(g)}$$

- (ii)  $\text{NOCl}_{2(g)} + \text{NO}_{(g)} \longrightarrow 2\text{NOCl}_{(g)}$
- (a) Write the overall reaction. (b) Identify reaction intermediate.
- (c) What is the molecularity of each step ? (3 marks) Solution : Given :
  - (i)  $NO_{(g)} + Cl_{2(g)} \longrightarrow NOCl_{2(g)}$
  - (ii)  $NOCl_{2(g)} + NO_{(g)} \longrightarrow 2NOCl_{(g)}$
  - (a) Overall reaction is obtained by adding both the reactions  $2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{2(g)}$
  - (b) The reaction intermediate is NOCl<sub>2</sub>, since it is formed in first step and consumed in the second step.
  - (c) Since the first step is slow and rate determining step, the molecularity is two.

Since the second step is a fast step its molecularity is not considered.

(6) In a first order reaction, the concentration of reactant decreases from 20 mmol dm<sup>-3</sup> to 8 mmol dm<sup>-3</sup> in 38 minutes. What is the half-life of reaction? (3 marks)

**Solution :** Given :  $[A]_0 = 20 \text{ mmol } dm^{-3};$ [A]<sub>t</sub> = 8 mmol  $dm^{-3}; t = 38 \text{ min};$  $t_{1/2} = ?$ 

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$
  
=  $\frac{2.303}{38} \log_{10} \frac{20}{8}$   
=  $\frac{2.303}{38} \times 0.3979$   
=  $0.02411 \text{ min}^{-1}$   
 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.02411} = 28.74 \text{ min}$ 

Ans. Half-life period = 28.74 min.

(7) The half-life of a first order reaction is 1.7 hours. How long will it take for 20% of the reactant to react? (3 marks)

Solution : Given : 
$$t_{1/2} = 1.7$$
 hr;  $[A]_0 = 100$ ;  
 $[A]_t = 100 - 20 = 80$ ;  $t = ?$   
 $t_{1/2} = \frac{0.693}{k}$   
 $\therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.7} = 0.4076$  hr<sup>-1</sup>  
 $\therefore k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$   
 $\therefore t = \frac{2.303}{k} \log_{10} \frac{100}{80}$   
 $= \frac{2.303 \times 0.09691}{0.4076}$   
 $= 0.5476$  hr  
 $= 0.5476$  kr  
 $= 0.5476 \times 60$  min  
 $= 32.86$  min

Ans. Time required = t = 32.86 min.

(8) A first order reaction takes 40 minutes for 30% decomposition. Calculate its half-life. *(3 marks)* 

**Solution : Given :** t = 40 min;  $[A]_0 = 100$ ;  $[A]_t = 100 - 30 = 70$ ;  $t_{1/2} = ?$ 

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$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$
  
=  $\frac{2.303}{40} \log_{10} \frac{100}{70}$   
=  $\frac{2.303}{40} \log_{10} 1.4286$   
=  $\frac{2.303 \times 0.1549}{40}$   
=  $8.918 \times 10^{-3} \min^{-1}$   
 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3}} = 77.70 \min^{-3}$ 

Ans. Half-life period = 77.70 min.

(9) Show that the time required for 99.9% completion of a first order reaction is three times the time required for 90% completion.

(2 marks)

Solution : Given : For 99.9% completion, if  $[A]_0 = 100$ ,  $[A]_t = 100 - 99.9 = 0.1$ For 90% completion, if  $[A]_0 = 100$ ,  $[A]_t = 100 - 90 = 10$   $k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$  $\therefore t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$ 

If  $t_1$  and  $t_2$  are the times required for 99.9% and 90% completion of reaction respectively, then

$$\frac{t_1}{t_2} = \frac{\frac{2.303}{k} \log_{10} \frac{100}{0.1}}{\frac{2.303}{k} \log_{10} \frac{100}{10}}$$
$$= \frac{\log 1000}{\log 10}$$
$$= \log 10^3$$
$$= 3 \log 10 = 3$$
$$\therefore t_1 = 3t_2$$

**Ans.** Time required for 99.9% completion of a first order reaction is **three time** the time required for 90% completion of the reaction.

#### Additional Important Examples for Self-practice

1. For the reaction,

2NOBr<sub>(g)</sub>  $\longrightarrow$  2NO<sub>2(g)</sub> + Br<sub>2(g)</sub>, the rate law is rate = k[NOBr]<sup>2</sup>. If the rate of the reaction is 6.5 × 10<sup>-6</sup> mol L<sup>-1</sup> s<sup>-1</sup> when the concentration of NOBr is 2 × 10<sup>-3</sup> mol L<sup>-1</sup> what would be the rate constant for the reaction? (Ans.  $k = 1.625 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ )

2. For the reaction,

order in B.

 $2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$ , the rate law is rate  $= k [NO]^2 [H_2]$ . What is the order with respect to NO and H<sub>2</sub>? What is the overall order of the reaction? (Ans. Order with respect to NO = 2,

Order with respect to  $H_2 = 1$ , Overall order of the reaction = 3) 3. For the reaction,

 $2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$  in liquid bromine,  $N_2O_5$  disappears at a rate of 0.02 moles dm<sup>-3</sup> sec<sup>-1</sup>. At what rate NO<sub>2</sub> and O<sub>2</sub> are formed? What would be the rate of reaction?

(Ans. Rate of formation of  $NO_2 = 0.04 \text{ M s}^{-1}$ ;

Rate of formation of  $O_2 = 0.01 \text{ M s}^{-1}$ ; Rate of reaction = 0.02 M s<sup>-1</sup>) 4. The rate of the reaction,  $A + B \rightarrow P$  is  $3.6 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ when  $[A] = 0.2 \text{ moles dm}^{-3}$  and  $[B] = 0.1 \text{ moles dm}^{-3}$ . Calculate the rate constant if the reaction is first order in A and second

(Ans. 18  $M^{-2} s^{-1}$ )

5. Consider a reaction, A + B → P. If the concentration of A is doubled with [B] being constant, the rate of the reaction doubles. If the concentration of A is tripled and that of B is doubled, the rate increases by a factor 6. What is order of the reaction with respect to each reactant? Determine the overall order of the reaction.

(Ans. Order with respect to A = 1;

Order with respect to B = 1, Overall order = 2)

6. The half-life of first order reaction is 990 s. If the initial concentration of the reactant is 0.08 mol dm<sup>-3</sup>, what concentration would remain after 35 minutes? (Ans. 0.0184 mol dm<sup>-3</sup>)

- 7. In a first order reaction 60% of the reactant decomposes in 45 minutes. Calculate the half-life for the reaction. (Ans.  $t_{1/2} = 34$  min)
- Following data were obtained during the first order decomposition of SO<sub>2</sub>Cl<sub>2</sub> at the constant volume.

 $\begin{array}{rcl} \mathrm{SO}_2\mathrm{Cl}_{2(g)} &\longrightarrow & \mathrm{SO}_{2(g)} + \mathrm{Cl}_{2(g)} \\ \mathrm{Time/s} & & \mathrm{Total \ pressure/bar} \\ 0 & & 0.5 \\ \mathrm{100} & & 0.6 \end{array}$ 

Calculate the rate constant of the reaction. (Ans.  $k = 2.23 \times 10^{-3} \text{ s}^{-1}$ )

- 9. Consider the reaction 2A + 2B → C + 2D. If the concentration of A is doubled at constant [B], the rate of the reaction increases by a factor 4. If the concentration of B is doubled at constant [A], the rate is doubled. What is the rate law? (Ans. Rate law : Rate = k[A]<sup>2</sup>[B])
- 10. The rate law for the reaction, A + B → products is rate = k [A][B]<sup>2</sup>. The rate of the reaction at 25 °C is found to be 0.25 M/s when [A] = 1.0 M and [B] = 0.2 M. Calculate the rate constant k at this temperature.

(**Ans.** Rate constant  $= k = 6.25 \text{ M}^{-2} \text{s}^{-1}$ )

11. Consider the reaction,

 $2H_{2(g)} + 2NO_{(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$ 

The rate of the reaction doubles if the concentration of H<sub>2</sub> is doubled. If the concentration of NO is doubled the rate increases by a factor 4. Write the rate law. (Ans. Rate law : Rate = k [H<sub>2</sub>][NO]<sup>2</sup>)