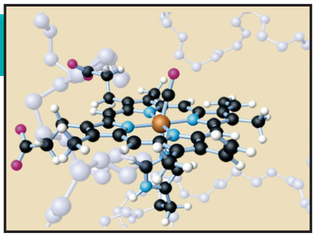
21

Catalysis

CHAPTER



KEY CONCEPTS AND EQUATIONS

CATALYST AND ITS TYPES

A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the reaction. This process is called catalysis. There are two main types of catalysis :

HOMOGENEOUS CATALYSIS

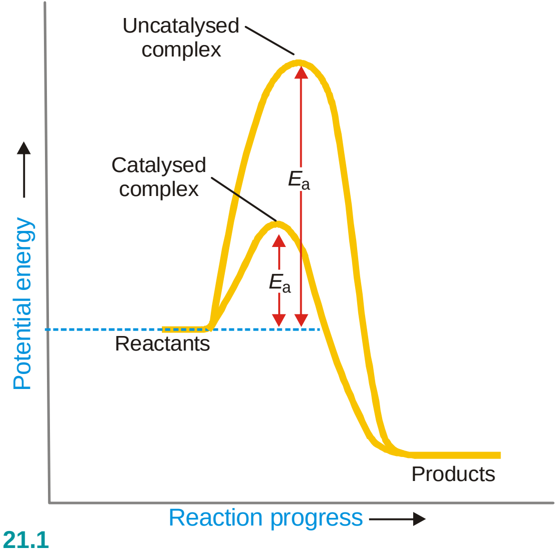
In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) phase.

HETEROGENEOUS CATALYSIS

In heterogeneous catalysis, the catalyst is in a different physical phase from the reactants.

ACTIVATION ENERGY AND CATALYSIS

Activation energy is defined as the minimum amount of energy required to cause a chemical reaction. A catalyst lowers the activation energy of the reaction by providing a new pathway as shown in Fig. 21.1.



■ **Figure 21.1**
Role of a catalyst.

ARRHENIUS EQUATION

Arrhenius suggested a simple relationship between the rate constant, *k*, for a reaction and the temperature of the system

$$k = A e^{-E_a/RT}$$

where E_a is the activation energy, *R* is the gas constant, *T* is absolute temperature and *A* is an experimentally determined quantity.

Taking natural logarithms, we have

$$\ln k = \frac{-E_a}{RT} + \ln A$$

or

$$\log k = \frac{-E_a}{2.303RT} + \log A$$

If k_1 and k_2 are the values of rate constants at temperature T_1 and T_2 , we have

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Arrhenius equation is used to calculate the activation energy, E_a, if the experimental value of rate constant, *k* is known.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. In the Arrhenius equation for a certain reaction, the value of *A* and E_a (activation energy) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes ?

SOLUTION : (i) To calculate the value of rate constant k

Formula used

$$k = \frac{0.693}{t_{½}}$$

Quantities given

$$t_{½} = 10 \text{ min} = 10 \times 60 \text{ sec} = 600 \text{ sec}$$

Substitution of values

$$k = \frac{0.693}{600 \text{ sec}} = 1.155 \times 10^{-3} \text{ sec}^{-1}$$

(ii) To calculate the temperature

Formula used

$$K = A e^{-E_a/RT}$$

Quantities given

$k = 1.155 \times 10^{-3}$ sec^{-1} $\quad$ $R = 8.314\ J$ $\quad$ $E_a = 98.6$ kJ

$A = 4 \times 10^{13}$ sec^{-1} $\quad$ $= 98.6 \times 10^3$ J

Substitution of values

$$\log(1.155 \times 10^{-3}) = -\frac{98.6 \times 10^3 \text{ J}}{2.303 \times 8.314 \text{ J} \times T} + \log(4 \times 10^{13})$$

$$-2.9374 = -\frac{5149.59}{T} + 13.6021$$

$$-16.5395 = -\frac{5149.59}{T}$$

or $$T = \frac{5149.59}{16.5395}$$

$$= \mathbf{311.35\ K}$$

SOLVED PROBLEM 2. From the following data for the reaction between A and B

$$2A \longrightarrow B$$

A (mol L^{-1})	B (mol L^{-1})	Initial rate at 300 K	Initial rate at 320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-5}	1.0×10^{-2}	–

Calculate the energy of activation and the pre-exponential factor.

SOLUTION : (i) To calculate rate constants (k_1) at 300 K and (k_2) at 320 K

Formula used

$$\textit{Rate constant} = \frac{Rate}{[A]^2[B]}$$

Quantities given

Rate at 300 K = 5.0×10^{-4} *Rate* at 320 K = 2×10^{-3}

$[A] = 2.5 \times 10^{-4}$ $[B] = 3.0 \times 10^{-5}$

Substitution of values

$$\textit{Rate constant } k_1 \textit{ at 300 K} = \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 \times (3.0 \times 10^{-5})}$$

$$= 2.66 \times 10^{8}$$

$$\textit{Rate constant } k_2 \textit{ at 320 K} = \frac{2 \times 10^{-3}}{(2.5 \times 10^{-4})^2 \times (3.0 \times 10^{-5})}$$

$$= 1.066 \times 10^{9}$$

(ii) To calculate the energy of Activation.

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Quantities given

$k_1 = 2.66 \times 10^{8}$ $k_2 = 1.066 \times 10^{9}$ $R = 8.314$ J mol^{-1} K^{-1}

$T_1 = 300$ K $T_2 = 320$ K

Substitution of values

$$\log \frac{1.066 \times 10^{9}}{2.66 \times 10^{8}} = \frac{Ea}{2.303 \times 8.314}\left[\frac{320 - 300}{320 \times 300}\right]$$

or $$E_a = \frac{0.6028 \times 2.303 \times 8.314 \times 320 \times 300}{20}$$

$$= \mathbf{5.5401 \times 10^{4}\ J}$$

(iii) To calculate pre-exponential factor

Formula used

$$k = A\,e^{-E_a/RT}$$

or
$$\log k = \log A - \frac{E_a}{2.303\,R\,T}$$

Quantities given

$k = 2.66 \times 10^8$ $\qquad$ $E_a = 5.5401 \times 10^4$ J

$R = 8.314$ J $\qquad$ $T = 300$ K

Substitution of values

$$\log\ 2.66 \times 10^8 = \log\ A - \frac{5.5401 \times 10^4}{2.303 \times 8.314 \times 300}$$

$$8.4249 = \log A - 9.6448$$

or
$$\log A = 18.6697$$

or
$$A = \text{Antilog } 18.0697$$

$$= \mathbf{1.175 \times 10^{18}}$$

SOLVED PROBLEM 3. At 380 °C, the half life period for the first order decomposition of H_2O_2 is 360 min. The rate constant at 450 °C is 6.81 × 10^{-2} min^{-1}. Calculate the energy of activation of the reaction.

SOLUTION : (i) To calculate the rate constant k_1 at 380 °C

Formula used

$$k_1 = \frac{0.693}{t_{½}}$$

Quantity given

$$t_{½} = 360 \text{ min}$$

Substitution of values

$$k_1 = \frac{0.693}{360 \text{ min}}$$

$$= 1.925 \times 10^{-3} \text{min}^{-1}$$

(ii) To calculate the energy of activation

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Quantities given

$k_2 = 6.81 \times 10^{-2}\ \text{min}^{-1}$ $\qquad$ $k_1 = 1.925 \times 10^{-3}\ \text{min}^{-1}$

$T_2 = 450 + 273 = 723$ K $\qquad$ $T_1 = 380 + 273 = 653$ K $\qquad$ $R = 8.314$ J

Substitution of values

$$\log \frac{6.81 \times 10^{-2}}{1.925 \times 10^{-3}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{723 - 653}{723 \times 653}\right]$$

$$1.5487 = \frac{E_a}{2.303 \times 8.314} \times \frac{70}{723 \times 653}$$

or
$$E_a = 200000 \text{ J} = \mathbf{200\ kJ}$$

ADDITIONAL PRACTICE PROBLEMS

1. For the reaction of hydrogen with iodine, the rate constant is 2.45×10^{-4} lit mol^{-1} at 302 °C and 0.950 lit mol^{-1} at 508 °C. Calculate the activation energy and the frequency factor for this reaction.

Answer. 150 kJ, 9.93×10^{-9} lit mol^{-1}

2. The rate constants for the decomposition of SO_2Cl_2 is 6.09×10^{-5} min^{-1} at 552.3 K. Calculate the frequency factor and rate constant at 600 if its activation energy is 210 kJ.

Answer. 4.42×10^{15} min^{-1} ; 2.31×10^{-3} min^{-1}

3. The rate constant for the first order decomposition of ethyl bromide at 800 K and 900 K are 0.0361 and 1.410 sec^{-1} respectively. Calculate the activation energy for the reaction.

Answer. 219 kJ

4. A first order reaction is half complete in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate the reaction rate constant at 300 K and the energy of activation.

Answer. 0.0231 min^{-1} ; 43.848 kJ

5. The specific reaction rate of a reaction is 1×10^{-3} min^{-1} at 300 K and 2×10^{-3} min^{-1} at 310 K. Calculate the energy of activation of the reaction.

Answer. 53.6 kJ

6. The rate constant of a first order reaction is 6 times the rate constant when the temperature is increased from 350 K to 410 K. Calculate the energy of activation for the reaction.

Answer. 35.63 kJ

7. The rate constants of a chemical reaction are 1×10^{-3} sec^{-1} and 2×10^{-3} sec^{-1} at 30 °C and 40 °C respectively. Calculate the energy of activation of the reaction.

Answer. 54.658 kJ

8. The decomposition of a compound follows first order kinetics and specific rate constants are 5.5×10^{-1} sec^{-1} and 9.2×10^{-3} sec^{-1} at 413 K and 458 K respectively. Calculate the energy of activation.

Answer. 2.37×10^{4} cal

9. Calculate the activation energy of a reaction for which the rate becomes double when the temperature is raised from 291 K to 311 K.

Answer. 50.80 kJ

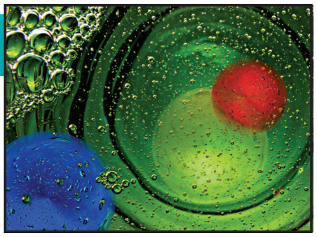
10. The specific reaction rate for a reaction increases by a factor of 4 if the temperature is raised from 27 °C to 47 °C. Calculate the activation energy of the reaction.

Answer. 55.693 kJ

22

The Colloids

CHAPTER



KEY CONCEPTS AND EQUATIONS

COLLOIDAL SOLUTIONS

A colloidal solution is an intermediate between true solution and suspension. In colloidal solution the size of the particle ranges from about 10 Å to 2000 Å.

LYOPHILLIC AND LYOPHOBIC SOLS

Lyophillic sols are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

Lyophobic sols are those in which the dispersed phase has no attraction for the medium or the solvent.

GOLD NUMBER

It is defined as the number of milligrams of a hydrophobic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10 percent sodium chloride solution.

EMULSIONS AND THEIR TYPES

An emulsion may be defined as a dispersion of finely divided liquid droplets in another liquid. Emulsions are of two types

(i) Oil in water type (O/W) and (ii) Water in oil type (W/O)

MACROMOLECULES

Colloidal solutions are formed by aggregation of atoms or molecules to give particles of colloidal size. There are substances which are composed of giant molecules and dissolve directly in a solvent to give colloidal solutions. Such giant molecules are called macromolecules.

MOLECULAR WEIGHT OF MACROMOLECULES

Two types of average molecular weights have been defined.

(i) Number average molecular weight

$$\overline{M}_n = \frac{\Sigma\, n_i M_i}{\Sigma\, n_i}$$

where $n_i M_i$ stands for the weight of macromolecules numbering n_i and having molecular weight M_i

(ii) Weight average molecular weight

$$\overline{M}_w = \frac{\Sigma\, m_i M_i}{m_i}$$

where m_i represent the mass of macromolecules having molecular weight M_i.

These two molecular weights are compared as follows :

$$\overline{M}_w > \overline{M}_n$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Consider a polymer mixture composed of 5 molecules of molar mass 1 kg mol^{-1}, 5 molecules of molar mass 2 kg mol^{-1}, 5 molecules of molar mass 3 kg mol^{-1} and 5 molecules of molar mass 4 kg mol^{-1}. Calculate (i) the number average molecular weight and (ii) weight average molecular weight.

SOLUTION : (i) To calculate the number average molecular weight

Formula used

$$\overline{M}_n = \frac{\Sigma\, n_i M_i}{\Sigma\, n_i} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + n_4 M_4}{n_1 + n_2 + n_3 + n_4}$$

Quantities given

$M_1 = 1$ kg mol^{-1} $M_2 = 2$ kg mol^{-1} $M_3 = 3$ kg mol^{-1} $M_4 = 4$ kg mol^{-1}

$n_1 = 5$ $n_2 = 5$ $n_3 = 5$ $n_4 = 5$

Substitution of values

$$\overline{M}_n = \frac{1 \times 5 + 2 \times 5 + 3 \times 5 + 4 \times 5}{5 + 5 + 5 + 5} \text{ kg mol}^{-1}$$

$$= \frac{5 + 10 + 15 + 20}{20} \text{ kg mol}^{-1}$$

$$= \mathbf{2.5 \text{ kg mol}^{-1}}$$

(ii) To calculate the weight average molecular weight

Formula used

$$\overline{M}_w = \frac{\Sigma\, m_i M_i}{\Sigma\, m_i} = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 + w_4 M_4}{m_1 + m_2 + m_3 + m_4}$$

Quantities gives

$M_1 = 1$ kg mol^{-1} $M_2 = 2$ kg mol^{-1} $M_3 = 3$ kg mol^{-1} $M_4 = 4$ kg mol^{-1}

$m_1 = 1$ $m_2 = 2$ $m_3 = 3$ $m_4 = 4$

Substitution of values

$$\overline{M}_w = \frac{1 \times 1 + 2 \times 2 + 3 \times 3 + 4 \times 4}{1 + 2 + 3 + 4} \text{ kg mol}^{-1}$$

$$= \frac{30}{10} \text{ kg mol}^{-1}$$

$$= \mathbf{3 \text{ kg mol}^{-1}}$$

SOLVED PROBLEM 2. A sample of polymer contains 10, 20, 30 and 40 percent molecules of the polymer with molecular weights 10000, 12000, 14000 and 16000. Calculate the mole fraction of each type of polymer molecule. Also calculate the number and weight average molecular weights of the polymer sample.

SOLUTION : **(i) To calculate the mole fraction of each type of polymer**

Formula used

$$\text{Mole fraction} \quad \overline{X}_i = \frac{\textit{Number of molecules of type i}}{\textit{Total number of molecules}}$$

Quantities given

No. of molecules of each type = 10, 20, 30 and 40

Total number of molecules = 100

Substitution of values

$$\text{Mole fraction of type } A = \frac{10}{100} = \mathbf{0.1}$$

$$\text{Mole fraction of type } B = \frac{20}{100} = \mathbf{0.2}$$

$$\text{Mole fraction of type } C = \frac{30}{100} = \mathbf{0.3}$$

$$\text{Mole fraction of type } D = \frac{40}{100} = \mathbf{0.4}$$

(ii) To calculate the number average molecular weight

Formula used

$$\overline{M}_n = \frac{\Sigma\, n_i M_i}{\Sigma\, n_i}$$

Quantities given

n_1 = 0.1 n_2 = 0.2 n_3 = 0.3 n_4 = 0.4

M_1 = 10000 M_2 = 12000 M_3 = 14000 M_4 = 16000

Substitution of values

$$\overline{M}_n = \frac{0.1 \times 1000 + 0.2 \times 12000 + 0.3 \times 14000 + 0.4 \times 16000}{0.1 + 0.2 + 0.3 + 0.4}$$

$$= 1000 + 2400 + 4200 + 6400$$

$$= \mathbf{14000}$$

(iii) To calculate the weight average molecular weight.

Formula used

$$\overline{M}_w = \frac{\Sigma\, X_i M_i^2}{\Sigma\, M_i}$$

$$= \frac{0.1 \times (10000)^2 + 0.2 \times (12000)^2 + 0.3 \times (14000)^2 + 0.4 \times (16000)^2}{14000}$$

$$= \frac{10^7 + 2.88 \times 10^7 + 5.88 \times 10^7 + 10.24 \times 10^7}{14000}$$

$$= \frac{20 \times 10^7}{14000}$$

$$= \mathbf{14286}$$

ADDITIONAL PRACTICE PROBLEMS

1. The following distribution of molecular weights has been found in a polymer sample

n_i	5	10	10	10	20	5	5
M_i	1000	2000	5000	10000	12000	15000	20000

Calculate the number average weight of the polymer.

Answer. 19461

2. A sample of polymer contain 5, 25, 40, and 30 percent molecules of the polymer with molecular weights 5000, 6000, 7000, and 8000. What is the mole fraction of each type of polymer ? Also calculate the number average molecular weight of polymer sample.

Answer. 0.05, 0.025, 0.40 and 0.3 ; 6950

3. A sample of polymer contains 100 molecules having molecular weight 10^3 each and 200 molecules with molecular weight 10^4 each and 200 molecules with molecular weight 10^5 each, Calculate the number average and weight average molecular weight.

Answer. 44000, 91000

4. Calculate the weight average molecular weight of a polymer containing equal number of particles with molecular weights 5000 and 10000.

Answer. 8333

5. Calculate number average molecular weight of a given sample of a polymer having 1000 molecules of 5000, 500 molecules of 4000 and 200 molecules of 3000 molecular weights.

Answer. 4470

6. A suspension contains equal masses of particles with molecular weight 20,000 and 40,000. Calculate number and weight average molecular weights of the suspension.

Answer. 26,667 and 30,000

7. There are two polymers A and B. A consists of equal number of molecular masses 10,000 and 30,000. B consists of equal number of molecular masses 15,000 and 35,000. Calculate the number average and mass average molecular mass for each polymer.

Answer. 20,000 and 25,000 ; 25,000 and 29,000

8. A sample of polymer contains 0.5 mole fraction with molecular weight 100,000 and 0.5 mole fraction with molecular weight 200,000. Calculate the average molecular weight of the polymer.

Answer. 150,000 and 166,667

9. Calculate the number average molecular weight of a sample of nylon having 1000 molecules of 5000 ; 2000 molecules of 6000 and 4000 molecules of 1000 molecular weight.

Answer. 3000

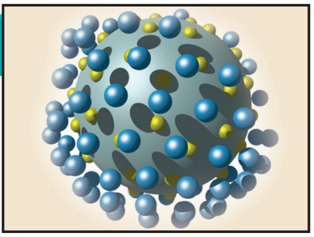
10. Calculate weight average molecular weight of a sample containing equal number of particles with molecular weight 10,000 and 20,000.

Answer. 16667

23

Adsorption

CHAPTER



KEY CONCEPTS AND EQUATIONS

ADSORPTION

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption.

PHYSICAL ADSORPTION

It is due to the gas molecules being held to the solid surface by vander Waal's attractive forces.

CHEMICAL ADSORPTION

It is due to the gas molecules being held to the solid surface by chemical bonds.

ADSORPTION ISOTHERMS

The relationship between the equilibrium pressure and its amount absorbed on the solid absorbent at any constant temperature is called an Adsorption Isotherm.

FREUNDLICH ADSORPTION ISOTHERM

The relation between the amount of gas adsorbed and its pressure is

$$w/m = kp^{1/n}$$

where w is the mass of the gas adsorbed on a mass m of adsorbent at a pressure p, k and n are constants depending upon the nature of the gas and adsorbent and on temperature.

LANGMUIR ADSORPTION ISOTHERM

The relation between the amount of gas adsorbed and its pressure is also given by

$$x = K' \frac{KP}{1+KP}$$

where K' is a constant, K is adsorption constant and P is the pressure of the gas.

Langmuir adsorption isotherm holds good at low pressures but fails at high pressures.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. 2.5 g of oxygen is adsorbed on 1.5 g of metal powder at 27 °C and 0.7 atm. Express the mass, number of moles and volume of oxygen at 27 °C, 0.7 atm and at NTP adsorbed per gram of the adsorbent.

SOLUTION :

Mass of adsorbate = 2.5 g

Mass of adsorbate = 1.5 g

$$\text{Mass of adsorbate per gram of adsorbent} = \frac{2.5\text{ g}}{1.5\text{ g}} = \mathbf{1.67}$$

$$\text{Number of moles of adsorbate per gram of adsorbent} = \frac{1.67}{32} = \mathbf{0.052}$$

$$\text{Volume of 1.67 g of } O_2 \text{ at } 27\ ^{o}\text{C and 0.7 atm} = \frac{0.052 \times 82 \times 300}{0.7}$$

$$= \mathbf{1827.4\ ml}$$

$$\text{Volume of 1.67 g of } O_2 \text{ at 273 K and 1 atm} = \frac{0.052 \times 82 \times 273}{0.7}$$

$$= \mathbf{1662.9\ ml}$$

SOLVED PROBLEM 2. The adsorption of a gas on a metal powder obeys Langmuir equation. The following experimental results have been obtained.

p (torr)	1	5	10	30	70	150
x/m	0.75	1.50	1.71	1.89	1.95	1.98

Determine the parameters *a* and *b* of the Langmuir equation.

SOLUTION : (i) To calculate the value of *m/x* and 1/p.

m/x	1.333	0.666	0.585	0.529	0.513	0.505
1/ p (torr^{-1})	1	0.2	0.1	0.033	0.014	0.0066

On plotting *m/x* against *1/ p*, we get a straight line whose slope is 0.83 torr and intercept = 0.5.

(ii) To calculate the value of a and b

Thus $1/a = 0.83$ torr or $a = \mathbf{1.2\ torr^{-1}}$

$b/a = 0.5$ and $b = \mathbf{0.6\ torr^{-1}}$

ADDITIONAL PRACTICE PROBLEMS

1. 4 g of a substance absorbs 87.5 ml of O_2 at 450 torr at 37 °C. Calculate *x/m* in mol per gram.

Answer. 5.265×10^{-4} mol g^{-1}

2. 100 ml of 0.3 M acetic acid is shaken with 0.8 g of wood charcoal. The final concentration of the solution after adsorption is 0.125 M. Calculate the weight of acetic acid adsorbed per gram of carbon.

Answer. 1.31 g

3. Five grams of a catalyst absorb 400 cm^3 of N_2 at STP to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 Å.

Answer. 344 m^2 g^{-1}

4. Charcoal absorbs a solute from its aqueous solution and obeys the Freundlich isotherm. The following data were obtained :

Equilibrium Conc $\times 10^2$ *M*	2.0	4.0	6.0	8.0
x/m	0.185	0.290	0.364	0.428

Determine the values of *k* and *n*.

Answer. $k = 206$; $n = 0.616$

5. Four gram of a gas is adsorbed on 1.5 g of metal powder at 300 K and 0.7 atm. Calculate the volume of the gas at STP adsorbed per gram of adsorbent.

Answer. 2052.5 m

6. 10.0 g of oxygen is adsorbed on 2.5 g of metal powder at 273 K and 1 atm pressure. Calculate the volume of the gas adsorbed per gram of adsorbent.

Answer. 2798.25 ml

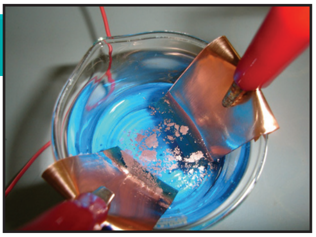
7. For an adsorbent – adsorbate system obeying the Langmuir adsorption isotherm, $a = 0.48$ bar^{-1} and $b = 0.16$ bar^{-1}. At what pressure will 50 % of the surface be covered ?

Answer. 1.25 bar

24

Electrolysis and Electrical Conductance

CHAPTER



KEY CONCEPTS AND EQUATIONS

ELECTROLYSIS AND ELECTRICAL UNITS

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is called Electrolysis. On passing electric current the ions move towards the oppositely charged electrodes where they get discharged either by losing electron or by gaining electrons. As a result of this chemical reaction takes place.

Coulomb

It is a unit of quantity of electricity. When 1 ampere current is passed for one second, the quantity of electricity is called one coulomb.

Ampere

It is a unit rate of flow of electicity. It is that current which will deposit 0.00118 g of silver in one second.

FARADAY'S LAWS OF ELECTROLYSIS

First law

The amount of a given substance liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution *i.e.*

$$m \;\alpha\; Q$$

or $$m \;\alpha\; I \times t \qquad [\because\; Q = I \times t]$$

or $$m = Z \times I \times t$$

where m is the mass of substance deposited in grams, I the strength of current in amperes, t the time in seconds for which the current has been passed and Z is a constant called Electrochemical equivalent.

If $I = 1$ ampere, $t = 1$ second, then

$$m = Z$$

Thus the electrochemical equivalent is the amount of a substance deposited by 1 ampere current passing for 1 second (*i.e.* one coulomb). The quantity of electricity required to liberate one gram equivalent of a substance is called Faraday, denoted by F and 1 F = 96500 coulombs.

Second law

When the same quantity of electricity passes through solution of different electrolytes, the amounts of substances liberated at the electrodes are directly proportional to their chemical equivalents (equivalent weight). *i.e.*

$$\frac{\text{mass of substances A deposited}}{\text{mass of substances B deposited}} = \frac{\text{Eq.Wt. of substance A}}{\text{Eq. Wt. of substance B}}$$

CONDUCTANCE OF ELECTROLYTES

The solution of electrolytes conduct electricity by the movement of ions to oppositely charged electrodes on passing electric current. The power of electrolytes to conduct electrical current is called conductivity or conductance. Electrolytes obey Ohm's law like metallic conductors. According to this law, the current I flowing through a metallic conductor is given by

$$I = \frac{E}{R}$$

where E is the potential difference at two ends and R is the resistance measured in ohms (Ω). The resistance of a conductor is proportional to its length, l, and inversely proportional to its area of cross-section, A. That is

$$R \propto \frac{l}{A}$$

or

$$R = \rho \times \frac{l}{A}$$

where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. We can also write

$$\rho = R \times \frac{A}{l}$$

If $l = 1$ cm, $A = 1$ sq cm then

$$\rho = R$$

Thus the specific resistance of a conductor is the reistance in ohms which one centimeter cube of it offers to the passage of electricity.

Specific conductance and its units

The reciprocal of specific resistance is called specific conductance or specific conductivity. It is defined as the conductance of one centimeter cube of a solution of an electrolyte. It is denoted by κ (Kappa). The

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

$$= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1}\text{cm}^{-1}$$

Equivalent conductance and its units

It is the conductance of an electrolyte by dissolving one gram-equivalent of it in V cm^3 of water. It is denoted by Λ. It is equal to the product of the specific conductance κ and the volume in cm^3 containing 1 gram-equivalent of the electrolyte at the dilution V. Thus

$$\Lambda = \kappa \times V$$

If an electrolyte contains N grams equivalents in 1000 cm^3 of the solution, the volume containing l g-equivalent will be 1000 N. Thus

$$\begin{aligned}\Lambda &= \frac{\kappa \times 1000}{N}\\ &= \kappa \times V\\ &= \frac{1}{R} \times \frac{l}{A} \times V \qquad \left[\because \kappa = \frac{1}{R} \times \frac{l}{A}\right]\\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{g eqvt}}\\ &= \mathbf{ohm^{-1}\ cm^2\ \ g\ eqvt^{-1}}\end{aligned}$$

Molar conductance and its units

The conductance of all ions produced by one mole of an electrolyte when dissolved in a certain volume V cm$^{3.}$ It is denoted by μ and is given by

$$\mu = \kappa \times V$$

where V is the volume of the solution in cm^3 containing 1 mole of the electrolyte.

$$\begin{aligned}\mu &= \frac{1}{R} \times \frac{l}{A} \times V \qquad \left[\because \kappa = \frac{1}{R} \times \frac{l}{A}\right]\\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{mol}}\\ &= \text{ohm}^{-1}\ \text{cm}^2\text{mol}^{-1}\end{aligned}$$

Degree of Dissociation

The degree of dissociation of a weak electrolyte is given by the conductance ratio *i.e.*

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

where Λ is the equivalent conductance at a given concentration and Λ_∞ is the equivalent conductance at zero concentration (infinite dilution).

Cell constant and its units

The ratio l / a is called the cell constant *i.e.*

$$\begin{aligned}\text{cell constant} &= \frac{l}{a}\\ &= \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}\end{aligned}$$

The cell constant is related in the specific conductance by the relation

$$\kappa = \frac{1}{R} \times \text{cell constant}$$

or

$$\text{cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. 0.5 normal solution of a salt placed between two platinum electrodes, 20 cm apart and of area of cross - section 4.0 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.

SOLUTION : (i) To calculate specific conductance

Formula used

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$R = 25$ ohms $\quad l = 20$ cm $\quad a = 4.0$ sq cm

Substitution of values

$$\kappa = \frac{1}{25 \text{ ohms}} \times \frac{20 \text{ cm}}{4.0 \text{ sq cm}}$$

$$= 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$$

(ii) To calculate equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$\kappa = 0.2 \text{ ohm}^{-1}\text{cm}^{-1}$ $\quad N = 0.5$ eqvt

Substitution of values

$$\text{Equivalent conductance} = \frac{0.2 \text{ ohm}^{-1}\text{cm}^{-1} \times 1000 \text{ cm}^3}{0.5 \text{ eqvt}}$$

$$= \mathbf{400 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}}$$

SOLVED PROBLEM 2. The resistance of N/10 solution is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution. Cell constant = 1.15 cm^{-1}

SOLUTION : To calculate specific conductance

Formula used

$$\kappa = \frac{l}{R} \times \textit{cell constant}$$

Quantities given

$R = 2.5 \times 10^3$ ohms $\quad$ *cell constant* = 1.15 cm^{-1}

Substitution of values

$$\kappa = \frac{1}{2.5 \times 10^3 \text{ ohm}} \times 1.15 \text{ cm}^{-1}$$

$$= 4.60 \times 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$$

(ii) To calculate equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$\kappa = 4.60 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ $\quad N = 0.1 \text{ eqvt}^{-1}$

Substitution of values

$$\text{Equivalent conductance} = \frac{4.60 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.1 \text{ eqvt}^{-1}}$$

$$= \mathbf{4.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}}$$

SOLVED PROBLEM 3. In a particular cell, 0.01M solution of KCl gave a resistance of 15.0 ohm at 298 K while 0.01 M solution of HCl gave a resistance of 51.4 ohm at the same temperature. If the specific conductance of 0.01 M KCl is 0.1409 Sm^{-1} at 280 K, calculate the cell constant, specific conductance and equivalent conductance of the HCl solution.

SOLUTION : (i) To calculate cell constant

Formula used

$$\text{Cell constant} = \frac{\textit{Specific conductance of KCl solution}}{\textit{Observed conductance of KCl solution}}$$

Quantities given

$$\text{Specific conductance of KCl} = 0.1409\ \text{sm}^{-1}$$

$$\text{Observed conductance of KCl} = \frac{1}{\textit{Resistance}} = \frac{1}{15\ \text{ohm}} = 0.667\ \text{ohm}^{-1}$$

Substitution of values

$$\text{Cell constant} = \frac{0.1409\ \text{sm}^{-1}}{0.0667\ \text{ohm}^{-1}} = \mathbf{2.11\ cm^{-1}}$$

(ii) To calculate the specific conductance of 0.01 M HCl

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \textit{cell constant}$$

Quantities given

$R = 51.4$ ohm $\qquad$ *cell constant* $= 2.11\ \text{cm}^{-1}$

Substitution of values

$$\text{Specific conductance} = \frac{1}{51.4\ \text{ohm}} \times 2.11\ \text{cm}^{-1} = \mathbf{4.10 \times 10^{-2}\ ohm^{-1}\ cm^{-1}}$$

(iii) To calculate the equivalent conductance of 0.01 M HCl

Formula used

$$\text{Equivalent Conductance} = \frac{\textit{Specific conductance} \times 1000}{N}$$

Quantities given

Specific Conductance $= 4.10 \times 10^{-2}$ $\qquad$ $N = 0.01$ eqvt

Substitution of values

$$\text{Equivalent conductance} = \frac{4.10 \times 10^{-2} \times 1000\ \text{cm}^3}{0.01\ \text{eqvt}}$$

$$= \mathbf{41\ ohm^{-1}cm^{2}eqvt^{-1}}$$

SOLVED PROBLEM 4. The specific conductance of N/5 KCl solution at 25 ºC is 0.002780 mho. The resistance of the cell containing this solution is 500 ohm. Calculate the cell constant.

SOLUTION :

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \text{cell constant}$$

or $\qquad$ Cell constant = Specific conductance × Resistance

Quantities given

Specific conductance = 0.002780 mho $\qquad$ $R = 500$ ohm

Substitution of values

$$\text{Cell constant} = 0.002780 \text{ mho} \times 500 \text{ ohm}$$
$$= \mathbf{1.39}$$

SOLVED PROBLEM 5. If the equivalent conductance at infinite dilution of NaCl, HCl and CH_3COONa are 126.45, 426.16 and 91.0 ohm^{-1} respectively, find the equivalent conductance of acetic acid at infinite dilution.

SOLUTION :

Formula used

$$\lambda_{\infty}(CH_3COOH) = \lambda_{\infty}(HCl) + \lambda_{\infty}(CH_3COONa) - \lambda_{\infty}(NaCl)$$

Quantities given

$\lambda_{\infty}(HCl) = 426.16 \text{ ohm}^{-1}$ $\quad\lambda_{\infty}(CH_3COONa) = 91.0 \text{ ohm}^{-1}$ $\quad\lambda_{\infty}(NaCl) = 12.6.45 \text{ ohm}^{-1}$

Substitution of values

$$\lambda_{\infty}(CH_3COOH) = 426.16 \text{ ohm}^{-1} + 91.0 \text{ ohm}^{-1} - 126.45 \text{ ohm}^{-1}$$
$$= \mathbf{390.71 \text{ ohm}^{-1}}$$

SOLVED PROBLEM 6. The equivalent conductance of ammonium chloride at infinite dilution is 149.7 ; for sodium hydroxide it is 247.8 mho; and for sodium chloride is 126.45 mho at 25 ºC. Calculate the equivalent conductance at the same temperature.

SOLUTION :

Formula used

$$\lambda_{\infty}(NH_4OH) = \lambda_{\infty}(NH_4Cl) + \lambda_{\infty}(NaOH) - \lambda_{\infty}(NaCl)$$

Quantities given

$\lambda_{\infty}(NH_4Cl) = 149.7 \text{ mho}$ $\quad\lambda_{\infty}(NaOH) = 247.8 \text{ mho}$ $\quad\lambda_{\infty} NaCl = 126.45 \text{ mho}$

Substitution of values

$$\lambda_{\infty}(NH_4OH) = 149.7 \text{ mho} + 247.8 \text{ mho} - 126.45 \text{ mho}$$
$$= \mathbf{271.05 \text{ mho}}$$

SOLVED PROBLEM 7. The resistance of a 0.5 N solution of an electrolyte occupying a volume between two platinum electrodes which are 1.72 cm apart and have an area of 4.5 sq cm is 25 ohms. Calculate the equivalent conductance of the solution.

SOLUTION : (i) To calculate specific conductance

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$R = 25 \text{ ohm}$ $\quad l = 1.72 \text{ cm}$ $\quad a = 4.5 \text{ sq cm}$

Substitution of values

$$\text{Specific conductance} = \frac{1}{25 \text{ ohm}} \times \frac{1.72 \text{ cm}}{4.5 \text{ sq cm}}$$
$$= 0.015289 \text{ ohm}^{-1}\text{cm}^{-1}$$

(ii) To calculate equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{\textit{Specific conductance} \times 1000}{N}$$

Quantities given

Specific conductance = $0.15289 \text{ ohm}^{-1}\text{cm}^{-1}$ $N = 0.5$ eqvt

Substitution of values

$$\text{Equivalent conductance} = \frac{0.015289 \text{ ohm cm}^{-1} \times 1000 \text{ cm}^3}{0.5 \text{ eqvt}}$$

$$= \mathbf{30.57 \text{ ohm cm}^2\text{eqvt}^{-1}}$$

SOLVED PROBLEM 8. Following results were obtained by conductance measurements of potassium sulphate using the cell with cell constant 0.2281. The observed conductance of potassium sulphate solution is 3×10^{-3} mhos. The equivalent conductance of potassium sulphate solution is 140 mho cm^2. Calculate the concentration of potassium sulphate solution..

SOLUTION : (i) To calculate the specific conductance

Formula used

$$\text{Cell constant} = \frac{\textit{Specific conductance}}{\textit{Observed conductance}}$$

Quantities given

Cell constant = 0.2281 *Observed conductance* = 3×10^{-3} mhos

Substitution of values

$$0.2281 = \frac{\textit{Specific conductance}}{3 \times 10^{-3} \text{ mho}}$$

or
$$\text{Specific Conductance} = 3 \times 10^{-3} \text{ mho} \times 0.2281$$

$$= 0.6843 \times 10^{-3} \text{mho}$$

(ii) To calculate concentration of the potassium sulphate solution

Formula used

$$\text{Equivalent conductance} = \frac{\textit{Specific conductance} \times \textit{1000}}{N}$$

Quantities given

Specific conductance = 0.6843×10^{-3} mho Equivalent conductance = 140 mhos cm^2

Substitution of values

$$140 \text{ mhos cm}^2 \text{eqvt}^{-1} = \frac{0.6843 \times 10^{-3} \text{ mho} \times 1000 \text{ cm}^3}{N}$$

or
$$N = \frac{0.6843 \times 10^{-3} \times 1000}{140} \text{ eqvt}$$

$$= \mathbf{0.00488 \text{ eqvt}}$$

SOLVED PROBLEM 9. 0.1 N solution of sodium acetate was placed between two electrodes which were 0.72 cm apart and each has a cross-section 2.25 $\text{cm}^{2.}$ The resistance of solution was 52.40 ohms. Find the specific and equivalent conductance.

SOLUTION : (i) To calculate the specific conductance

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

R = 52.40 ohm l = 0.72 cm a = 2.25 cm^2

Substitution of values

$$\text{Specific conductance} = \frac{1}{52.40 \text{ ohm}} \times \frac{0.72 \text{ cm}}{2.25 \text{ cm}^2} = \mathbf{0.0061 \text{ ohm}^{-1} \text{ cm}^{-1}}$$

(ii) To calculate the equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{\textit{Specific conductance} \times 1000}{N}$$

Quantities given

Specific conductance $= 0.0061 \text{ ohm}^{-1} \text{ cm}^{-1}$ $\quad N = 0.1$ eqvt

Substitution of values

$$\text{Equivalent conductance} = \frac{0.0061 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.1 \text{ eqvt}}$$

$$= \mathbf{61\ ohm^{-1} cm^2 eqvt^{-1}}$$

SOLVED PROBLEM 10. 0.5 N NaCl is placed between two electrodes 1.5 cm apart and having an area of each 3.0 sq cm offered a resistance of 25.0 ohms. Calculate the equivalent conductance.

SOLUTION : (i) To calculate the specific conductance

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$R = 25.0$ ohm $\quad l = 1.5$ cm $\quad a = 3.0$ sq cm

Substitution of values

$$\text{Specific conductance} = \frac{1}{25.0 \text{ ohm}} \times \frac{1.5 \text{ cm}}{3.0 \text{ cm}^2}$$

$$= 0.020 \text{ ohm}^{-1} \text{ cm}^{-1}$$

(ii) To calculate the equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{\textit{Specific conductance} \times 1000}{N}$$

Quantities given

Specific conductance $= 0.020 \text{ ohm}^{-1}\text{cm}^{-1}$ $\quad N = 0.5$ eqvt

Substituting of values

$$\text{Equivalent conductance} = \frac{0.020 \text{ ohm}^{-1}\text{cm}^{-1} \times 1000 \text{ cm}^3}{0.5 \text{ eqvt}}$$

$$= \mathbf{40\ ohm^{-1} cm^2\ eqvt^{-1}}$$

SOLVED PROBLEM 11. A conductance cell when filled with 0.05 solution of KCl records a resistance of 410.5 ohm at 25 ºC. When filled with calcium chloride solution (11g $CaCl_2$ in 500 ml) it records 990 ohms. If the specific conductance of 0.05M KCl solution is 0.00189 mho cm^{-1}, calculate (i) the cell constant, (ii) specific conductance (iii) molecular conductance of $CaCl_2$.

SOLUTION : (i) To calculate the cell constant

Formula used

$$\text{Cell constant} = \frac{\textit{Specific conductance}}{\textit{Observed conductance}}$$

Quantities given

Specific conductance $= 0.00189 \text{ mho cm}^{-1}$

$$\text{Observed conductance} = \frac{1}{R} = \frac{1}{410.5 \text{ ohm}}$$

Substitution of values

$$\text{Cell constant} = \frac{0.00189 \text{ mho cm}^{-1}}{1 / 410.5 \text{ ohm}} = \mathbf{0.7758\ cm^{-1}}$$

(ii) To calculate specific conductance of $CaCl_2$ Solution

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \textit{cell constant}$$

Quantities given

$R = 990 \text{ ohm}$ $\qquad$ *cell constant* $= 0.7758 \text{ cm}^{-1}$

Substitution of values

$$\text{Specific conductance} = \frac{1}{990 \text{ ohm}} \times 0.7758 \text{ cm}^{-1}$$
$$= \mathbf{0.000784 \text{ ohm}^{-1} \text{ cm}^{-1}}$$

(iii) To calculate molar conductance of $CaCl_2$

Formula used

$$\text{Molar conductance, } \mu = \frac{\kappa \times 1000}{M}$$

Quantities given

$\kappa = 0.000784 \text{ ohm}^{-1} \text{ cm}^{-1}$ $\qquad$ $M = \dfrac{22 \text{ g}}{111 \text{ g mol}^{-1}} = 0.198 \text{ mol}$

Substitution of values

$$\mu = \frac{0.000784 \text{ ohm}^{-1} \text{cm}^{-1} \times 1000 \text{ cm}^3}{0.198 \text{ mol}}$$
$$= \mathbf{3.95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

SOLVED PROBLEM 12. From the following data calculate the equivalent conductance (Λ_0) for NH_4OH

$Ba(OH)_2$; $\Lambda_0 = 228.3$ mhos
$BaCl_2$; $\Lambda_0 = 120.3$ mhos
NH_4Cl ; $\Lambda_0 = 129.8$ mhos

SOLUTION :

Formula used

$$\Lambda_0(NH_4OH) = \Lambda_0(Ba(OH)_2) + 2 \times \Lambda_0(NH_4Cl) - \Lambda_0(BaCl_2)$$

Quantities given

$\Lambda_0[Ba(OH)_2] = 228.3$ mhos $\qquad$ $\Lambda_0(NH_4Cl) = 129.8$ mhos $\qquad$ $\Lambda_0(BaCl_2) = 120.3$ mhos

Substituting of values

$$\Lambda_0(NH_4OH) = 228.3 + 2 \times 129.8 - 120.3$$
$$= 488.4 - 120.3$$
$$= \mathbf{367.4 \text{ mhos}}$$

SOLVED PROBLEM 13. The resistance of a N/100 Solution of an electrolyte was found to be 210 ohm at 25 ºC. Calculate the equivalent conductance of the solution at 25 ºC. (Cell constant = 0.88)

SOLUTION : (i) To calculate the specific conductance

Formula used

$$\kappa = \frac{1}{R} \times \textit{Cell constant}$$

Quantities given

$R = 210 \text{ ohm}$ $\qquad$ *cell constant* $= 0.88 \text{ cm}^{-1}$

Substitution of values

$$\kappa = \frac{1}{210\text{ ohm}} \times 0.88\text{ cm}^{-1}$$
$$= 0.004190\text{ ohm}^{-1}\text{cm}^{-1}$$

(ii) To calculate the equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$\kappa = 0.004190\text{ ohm}^{-1}\text{cm}^{-1}$ $\qquad N = \frac{1}{100}\text{ eqvt} = 0.01\text{ eqvt}$

Substitution of values

$$\text{Equivalent conductance} = \frac{0.004190\text{ ohm}^{-1}\text{cm}^{-1} \times 1000\text{ cm}^3}{0.01\text{ eqvt}}$$
$$= \mathbf{419\ ohm^{-1}\ cm^2\ eqvt^{-2}}$$

SOLVED PROBLEM 14. A conductance cell had a resistance of 165 ohms when filled with 0.02 molar KCl solution at 25 °C. For such solution specific conductance is 0.00277 mho cm^{-1}. The same cell filled with 0.01 molar NaCl had a resistance of 384 ohms. Calculate specific conductance and equivalent conductance of solution.

SOLUTION : (i) To calculate the cell constant.

Formula used

$$\text{Cell constant} = \frac{\textit{Specific conductance}}{\textit{Observed conductance}}$$

Quantities given

Specific conductance $= 0.00277\text{ mho cm}^{-1}$

Observed conductance $= \frac{1}{R} = \frac{1}{165\text{ ohm}} = 0.006061\text{ ohm}^{-1}$

Substitution of values

$$\text{Cell constant} = \frac{0.00277\text{ mho cm}^{-1}}{0.006061\text{ ohm}^{-1}} = 0.4570\text{ cm}^{-1}$$

(ii) To calculate the specific conductance of NaCl solution

Formula used

$$\kappa = \frac{1}{R} \times \textit{cell constant}$$

Quantities given

$R = 384$ ohms $\qquad$ *cell constant* $= 0.4570\text{ cm}^{-1}$

Substitution of values

$$\kappa = \frac{1}{384\text{ ohm}} \times 0.4570\text{ cm}^{-1}$$
$$= 0.001190\text{ ohm}^{-1}\text{ cm}^{-1}$$
$$= \mathbf{1.190 \times 10^{-3}\ ohm^{-1}cm^{-1}}$$

(iii) To calculate the equivalent conductance of 0.01M NaCl solution

Formula used

$$\text{Equivalent conductance} = \frac{\textit{Specific conductance} \times \textit{1000}}{N}$$

Quantities given

Specific conductance $= 1.190 \times 10^{-3}\text{ ohm}^{-1}\text{cm}^{-1}$ $\qquad N = 0.01\text{ M} = 0.01\text{ eqvt}$

Substitution of values

$$\text{Equivalent conductance} = \frac{1.190 \times 10^{-3}\,\text{ohm}^{-1}\text{cm}^{-1} \times 1000\,\text{cm}^3}{0.01\,\text{eqvt}}$$

$$= \mathbf{119\ ohm^{-1}cm^{-2}eqvt^{-1}}$$

SOLVED PROBLEM 15. The conductance of N/10 $AgNO_3$ solution taken in a cell with cell constant 0.9555 cm^{-1} is 0.0099 ohm^{-1}. Calculate (i) specific conductance (ii) equivalent conductance

SOLUTION : (i) To calculate specific conductance

Formula used

$$\kappa = \frac{1}{R} \times \text{Cell constant}$$

Quantities given

$\frac{1}{R} = 0.0099\ \text{ohm}^{-1}$ $\qquad$ *cell constant* $= 0.9555\ \text{cm}^{-1}$

Substitution of values

$$\kappa = 0.0099\ \text{ohm}^{-1} \times 0.9555\ \text{cm}^{-1}$$

$$= \mathbf{0.00946\ ohm^{-1}\ cm^{-1}}$$

(ii) To calculate equivalent conductance

Formula used

$$\text{Equivalent conductance} = \frac{Sp.\ conductance \times 1000}{N}$$

Quantities given

Sp. conductance = 0.00946 $ohm^{-1}cm^{-1}$ $\qquad$ $N = 1/10 = 0.1$ eqvt

Substitution of values

$$\text{Equivalent conductance} = \frac{0.00946\ \text{ohm}^{-1}\text{cm}^{-1} \times 1000\ \text{cm}^3}{0.1\ \text{eqvt}}$$

$$= \mathbf{94.6\ ohm^{-1}cm^{2}eqvt^{-1}}$$

SOLVED PROBLEM 16. The resistance of a cell containing 0.02 M KCl was found to be 175 ohms. The specific conductance of this solution is 27.7×10^{-4} ohm^{-1} cm^{-1} at 25 °C. An exactly 0.1M solution of another substance in the same cell had a resistance of 579 ohms. Calculate the equivalent conductance of this substance.

SOLUTION : (i) To calculate the cell constant

Formula used

$$\text{Cell constant} = \frac{Specific\ conductance}{Observed\ conductance}$$

Quantities given

Specific conductance $= 27.7 \times 10^{-4}\text{ohm}^{-1}\text{cm}^{-1}$

Observed conductance $= \frac{1}{R} = \frac{1}{175\ \text{ohm}} = 0.005714\ \text{ohm}^{-1}$

Substitution of values

$$\text{Cell constant} = \frac{27.7 \times 10^{-4}\ \text{ohm}^{-1}\ \text{cm}^{-1}}{0.005714\ \text{ohm}^{-1}} = 0.4847\ \text{cm}^{-1}$$

(ii) To calculate the specific conductance of the substance

Formula used

$$\kappa = \frac{1}{R} \times Cell\ constant$$

Quantities given

$R = 579$ ohms $\qquad$ *cell constant* $= 0.4847\ \text{cm}^{-1}$

Substitution of values

$$\kappa = \frac{0.4847\ \text{cm}^{-1}}{579\ \text{ohm}} = 0.000837\ \text{ohm}^{-1}\text{cm}^{-1}$$

(iii) To calculate the equivalent conductance of the substance

Formula used

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$\kappa = 0.000837\ \text{ohm}^{-1}\text{cm}^{-1}$ $\qquad$ $N = 0.01$ eqvt

Substitution of values

$$\text{Equivalent conductance} = \frac{0.000837 \times 1000\ \text{cm}^3}{0.01\ \text{eqvt}}$$

$$= \mathbf{83.7\ ohm^{-1}cm^{-2}\ eqvt^{-1}}$$

SOLVED PROBLEM 17. The specific conductance of N/50 KCl solution is 0.002765 $\text{ohm}^{-1}\text{cm}^{-1}$ at 25 ºC. If the resistance of the solution contained in the cell is 1000 ohms, calculate the cell constant.

SOLUTION :

Formula used

$$\text{Cell constant} = \frac{\textit{Specific conductance}}{\textit{Observed conductance}}$$

Quantities given

$$\text{Specific conductance} = 0.002765\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\text{Observed conductance} = \frac{1}{R} = \frac{1}{1000\ \text{ohm}} = 0.01\ \text{ohm}^{-1}$$

Substitution of values

$$\text{Cell constant} = \frac{0.002765\ \text{ohm}^{-1}\ \text{cm}^{-1}}{0.001\ \text{ohm}^{-1}}$$

$$= \mathbf{0.2765\ cm^{-1}}$$

SOLVED PROBLEM 18. Find specific conductivity of the solution if 0.5 M solution of a salt occupying a volume between two Pt electrodes 1.72 cm apart and of area 4.5 sq cm has a resistance of 15 ohms.

SOLUTION :

Formula used

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$R = 15$ ohm $\qquad$ $l = 1.72$ cm $\qquad$ $a = 4.5\ \text{cm}^2$

Substitution of values

$$\kappa = \frac{1}{15\ \text{ohm}} \times \frac{1.72\ \text{cm}}{4.5\ \text{cm}^2}$$

$$= \mathbf{0.02548\ ohm^{-1}\ cm^{-1}}$$

SOLVED PROBLEM 19. What will be the degree of ionisation of N/1000 acetic acid solution if its equivalent conductivity is 50 mhos and the value of equivalent conductivity at infinite dilution is 350 mhos ?

SOLUTION :

Formula used

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Quantities given

Λ_0 = 350 mhos $\qquad$ Λ = 50 mhos

Substitution of values

$$\alpha = \frac{50 \text{ mhos}}{350 \text{ mhos}} = \mathbf{0.142857}$$

SOLVED PROBLEM 20. Resistance of 0.01 M aqueous solution of an electrolyte at room temperature is 420 ohm and cell constant is 0.84 $\text{cm}^{-1.}$ Calculate the molar conductance.

SOLUTION : (i) To calculate the specific conductance

Formula used

$$\kappa = \frac{l}{R} \times \textit{Cell constant}$$

Quantities given

R = 420 ohm^{-1} $\qquad$ cell constant = 0.84 cm^{-1}

Subsitution of values

$$\kappa = \frac{1}{420 \text{ ohm}^{-1}} \times 0.84 \text{ cm}^{-1}$$

$$= 0.002 \text{ ohm cm}^{-1}$$

(ii) To calculate the molar conductance

Formula used

$$\text{Molar conductance, } \mu = \frac{\textit{Specific conductance} \times 1000}{\textit{Molarity}}$$

Quantities given

Specific conductance = 0.002 $\text{ohm}^{-1}\text{cm}^{-1}$ $\qquad$ *Molarity* = 0.01 M

Substitution of values

$$\mu = \frac{0.002 \text{ ohm}^{-1}\text{cm}^{-1} \times 1000 \text{ cm}^3}{0.01 \text{ M}}$$

$$= \mathbf{200 \ ohm^{-1} \ cm^2 \ mol^{-1}}$$

SOLVED PROBLEM 21. The equivalent conductance at infinite dilution (Λ_0) of HCl, CH_3COONa and NaCl are 426.16, 91.0 and 126.45 $\text{ohm}^{-1}\text{cm}^2\text{g eqvt}^{-1}$ respectively. Calculate Λ_0 of acetic acid.

SOLUTION :

Formula used

$$\Lambda_0 (CH_3COOH) = \Lambda_0 (CH_3COONa) + \Lambda_0 (HCl) - \Lambda_0 (NaCl)$$

Quantities given

$$\Lambda_0 (CH_3COONa) = 91.0 \text{ ohm}^{-1}\text{cm}^2\text{g eqvt}^{-1}$$

$$\Lambda_0 (HCl) = 426.16 \text{ ohm}^{-1}\text{cm}^2 \text{ g eqvt}^{-1}$$

$$\Lambda_0 (NaCl) = 126.45 \text{ ohm}^{-1}\text{cm}^2 \text{ g eqvt}^{-1}$$

Subsitution of values

$$\Lambda_0 (CH_3COOH) = 91.0 + \quad 426.16 - 126.45 \quad \text{ohm}^{-1}\text{cm}^2\text{g eqvt}^{-1}$$

$$= \mathbf{390.71 \ ohm^{-1}cm^2 \ g \ eqvt^{-1}}$$

SOLVED PROBLEM 22. Calculate the quantity of electricity that would be required to reduce 12.3 g nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 volts, how much energy will be consumed ?

SOLUTION : (i) To calculate the quantity of electricity

The reaction is

$$\underset{123\text{ g}}{C_6H_5NO_2} + \underset{6\text{g}}{6H^+} + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$$

Hydrogen required for the reduction of 123g of $C_6H_5NO_2$ = 6g

and Hydrogen required for the reduction of 12.3 g of $C_6H_5NO_2$ $= \dfrac{6\text{ g} \times 12.3\text{ g}}{123\text{ g}} = 0.6\text{ g}$

$$1\text{ g of Hydrogen} \equiv 96500\text{ coulombs}$$

$$\therefore \quad 0.6\text{ g of Hydrogen} = \frac{96500\text{ coulomb} \times 0.6\text{ g}}{1.0\text{ g}}$$

$$= 57900\text{ coulombs}$$

The quantity of electricity required for the reaction

$$= \frac{57900\text{ coulomb} \times 100}{50} \qquad [\because \text{ current efficiency} = 50\%]$$

$$= \mathbf{115800\ coulombs}$$

(ii) To calculate the energy consumed

$$\text{Total energy consumed} = 3\text{ volts} \times 115800\text{ coulombs}$$

$$= 347400\text{ J} \qquad [\because \text{ volt} \times \text{coulomb} = 1\text{ J}]$$

$$= \mathbf{347.4\ kJ}$$

SOLVED PROBLEM 23. An aqueous solution of NaCl on electrolysis gives $H_{2\,(g)}$, $Cl_{2\,(g)}$ and $NaOH_{(aq)}$ according to the reaction.

$$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightleftharpoons 2OH^-_{(aq)} + H_{2(g)} + Cl_{2\,(g)}$$

A direct current of 25 amperes with a current efficiency of 62% is passed through 20% litres of NaCl solution (20% by weight). How long will it take to produce 1 Kg of Cl_2 ? What will be the molarity of solution with respect to hydroxide ion ? (Assuming no loss due to evaporation).

SOLUTION : (i) To calculate time to produce 1 kg of Cl_2

Formula used

$$m = Z \times I \times t \qquad \text{where } Z = \frac{E}{96500}$$

or $$m = \frac{E}{96500} \times I \times t$$

Quantities given

m = 1000 g $\qquad E = 35.5\text{ g} \qquad I = \dfrac{25\text{ amp} \times 62}{100} = 15.5\text{ amp}$

Substitution of values

$$1000\text{ g} = \frac{35.5\text{g}}{96500} \times 15.5 \times t$$

or $$t = \frac{1000 \times 96500}{35.5 \times 15.5}\text{ sec}$$

$$= 175374\text{ sec}$$

$$= \mathbf{48.71\ hrs}$$

(ii) To calculate the molarity of solution with respect to OH^- ions.

$$\text{No of moles of } Cl_2 \text{ produced} = \frac{100\text{g}}{71 \text{ g mol}^{-1}} = 1.4085 \text{ moles}$$

$$\text{Amount of } OH^- \text{ released during the reaction} = 2 \times 1.4085 \text{ moles}$$

$$= 2.817 \text{ moles} \qquad [\because Cl_2 \equiv 2OH^-]$$

$$\text{Molarity of solution w.r.t. } OH^- \text{ ions} = \frac{2.817 \text{ moles}}{20 \text{ litres}}$$

$$= \mathbf{0.14085\ M}$$

SOLVED PROBLEM 24. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation :

$$CrO_{3(aq)} + 6H^+_{(aq)} + 6e^- \longrightarrow Cr_{(s)} + 3H_2O$$

Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 ampere current ?

SOLUTION : (ii) To calculate the amount of chromium that will be plated out

The reaction is

$$CrO_{3(aq)} + 6H^+_{(aq)} + 6e^- \longrightarrow Cr_{(s)} + 3H_2O$$

$$52\text{g of Cr} \equiv 6 \text{ Faradays}$$

$$= 6 \times 96500 \text{ coulombs}$$

$$\text{Thus } 6 \times 96500 \text{ coulomb of electricity produce Cr} = 52\text{g}$$

$$1 \text{ coulomb of electricity produce Cr} = \frac{52 \text{ g}}{6 \times 96500 \text{ coulomb}}$$

$$24000 \text{ coulombs of electricity produce Cr} = \frac{52\text{g} \times 24000 \text{ coulomb}}{6 \times 96500 \text{ coulomb}}$$

$$= \mathbf{2.15544\ g}$$

(ii) To calculate the time to plate out 1.5 g of chromium by using 12.5 ampere current

Formula used

$$m = Z \times I \times t$$

where

$$Z = \frac{52}{6 \times 96500} \qquad [\because \text{ Eq wt of Cr} = 52]$$

Quantities given

$m = 1.5$ g $\qquad Z = \dfrac{52}{6 \times 96500}\, g \qquad I = 12.5$ amp.

Substitution of values

$$1.5 \text{ g} = \frac{52 \text{ g} \times 12.5 \text{ amp} \times t}{6 \times 96500}$$

or

$$t = \frac{1.5 \times 6 \times 96500}{52 \times 12.5}$$

$$= \mathbf{1336.15\ sec}$$

SOLVED PROBLEM 25. An electric current of 2.0 ampere was passed through acidulated water for two hours. Calculate the volumes of hydrogen gas produced at STP. The electrochemical equivalent of hydrogen is 1×10^{-5} g.

SOLUTION : (i) To calculate the amount of H_2 liberated

Formula used

$$m = Z \times I \times t$$

Quantities given

$Z = 1 \times 10^{-5}$ g $\qquad I = 2.0$ ampere $\qquad t = 2 \times 60 \times 60$ sec

Substitution of values

$$m = 1 \times 10^{-5} \times 2.0 \times 7200 \text{ g}$$
$$= 0.144 \text{ g}$$

(ii) To calculate the volume of hydrogen gas at STP

$$1 \text{ mol of } H_2 = 22.4 \text{ litre at STP}$$
$$2 \text{ g of } H_2 = 22.4 \text{ litre at STP}$$
$$0.144 \text{ g of } H_2 = \frac{22.4 \text{ lit} \times 0.144 \text{ g}}{2 \text{ g}}$$
$$= \mathbf{1.612 \text{ lit}}$$

SOLVED PROBLEM 26. What current strength in ampere will be required to deposit 100 of silver from $AgNO_3$ solution in one hour ?

SOLUTION :

Formula used

$$m = Z \times I \times t$$

Quantities given

$t = 3600$ sec $\qquad m = 100$ g $\qquad Z = \dfrac{108 \text{ g}}{96500 \text{ C}}$

Substitution of values

$$100 \text{ g} = \frac{108 \text{ g}}{96500 \text{ C}} \times I \times 3600 \text{ sec}$$

or
$$I = \frac{100 \times 96500}{108 \times 3600} \text{ ampere}$$
$$= \mathbf{24.82 \text{ ampere}}$$

ADDITIONAL PRACTICE PROBLEMS

1. How many atoms of copper will be deposited from a solution of $CuSO_4 5H_2O$ by a current of 25 milliamperes for 100 sec ?

Answer. 7.797×10^{18} atoms of Cu

2. A current of 2.0 ampere is passed through 500 ml of 0.1 M solution of $ZnSO_4$ for 4 minutes with a current efficiency of 90%. Find out the molarity of Zn^{2+} after deposition of Zn assuming volume remain constant.

Answer. 0.0977 M

3. Calculate the quantity of electricity that will be required to produce 355 g chlorine gas by the electrolysis of a concentrated solution of NaCl. Also calculate the volume of hydrogen gas liberated at 27 ºC and 1 atm pressure during the process.

Answer. 10 F ; 123.07 lit

4. A current 4.0 amperes is passed for 8 hours between nickel electrodes in 500 ml of 2M solution of nickel nitrate. What will be the molarity of the solution at the end of electrolysis ?

Answer. 0.806 M

5. A solution of copper sulplate weighing 20g was electrolysed using 0.02 Faraday of electricity. Calculate the weight of the resulting solution.

Answer. 9.205 g

6. A current deposits 10 g of copper in 30 hours from a solution of Cu^{2+} ions. Calculate the strength of the current in amperes.

Answer. 0.2814 amp

7. How many grams of iodine are produced when a current of 8.52 mA flows through an aqueous solution of potassium iodide using platinum electrodes for 10 minutes ?

Answer. 0.00673 g

8. When molten lithium chloride, LiCl, is electrolysed, lithium metal is liberated at the cathode. How many grams of lithium are liberated when 5000C of charge passes through the cell ?

Answer. 0.360 g

9. A potential difference of 10 volts is applied to the ends of a column of 0.1 N $AgNO_3$ solution, 2 cm in diameter and 6 cm in length gives a current of 0.99 ampere. Calculate the specific conductance and equivalent conductance of the solution.

Answer. 0.18917 $ohm^{-1}cm^{-1}$; 1891.7 $ohm^{-1}cm^{-2}eqvt^{-1}$

10. Specific conductance of 0.1 N solution of an electrolyte is 0.02 $ohm^{-1}cm^{-1}$. Calculate its equivalent conductance.

Answer. 200 $ohm^{-1}cm^{2}eqvt^{-1}$

11. Specific conductance of 0.02 N KCl at 298 K is 0.002768 ohm^{-1} and it has resistance of 500 ohms. An 0.25 N solution of another salt kept in the same cell was found to have resistance of 300 ohms at 298 K. Calculate the cell constant and equivalent conductance of the salt solution.

Answer. 1.384; 18.45 $ohm^{-1}cm^{2}eqvt^{-1}$

12. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per reaction :

$$Mn^{2+}_{(aq)} + 2H_2O \longrightarrow MnO_{2\,(s)} + 2H^{+}_{(aq)} + H_{2\,(g)}$$

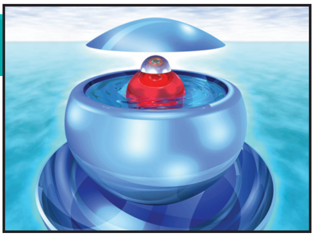
Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency.

Answer. 95.2%

25

CHAPTER

Theory of Electrolytic Dissociation



KEY CONCEPTS AND EQUATIONS

ARRHENIUS THEORY OF IONISATION

According to this theory an electrolyte on dissolution in water splits up into ions which reunite to form neutral molecules and there is a state of equilibrium between the undissociated molecules and the ions.

$$K = \frac{[A^+]\,[B^-]}{[AB]}$$

where K is called the Dissociation constant.

TRANSPORT NUMBER AND ITS DETERMINATION

The fraction of the total current carried by the cation or the anion is called Transport number. It is given by

$$t_+ = \frac{v_+}{v_+ + v_-} \qquad \text{and} \qquad t_- = \frac{v_-}{v_+ + v_-}$$

HITTORF'S METHOD

It is based on Hittorf 's rule – the loss of concentration around any electrode is proportional to the speed of the ion moving away from that electrode.

(i) When electrodes are unattackable

$$\textit{Transport number of } Ag^+ = \frac{\textit{Fall in concentration around anode in g eqvt}}{\textit{Amt. of Ag deposited in g eqvt}}$$

$$= \frac{d}{W}$$

(ii) When electrodes are attackable

$$\textit{Transport number of } Ag^+ = \frac{W - e}{W}$$

where W is the increase in concentration of Ag^+ ions if no Ag^+ ions had migrated from the anode and e is the increase in concentration of anodic solution.

MOVING BOUNDARY METHOD

It is based on the direct observation of migration of ions under the influence of applied potential.

$$t_{A+} = \frac{s \times l \times c}{n}$$

where l is distance through which the boundary moves, s the area of cross - section of the tube, $n = Q / F$, Q being the quantity of current passed and F stands for Faraday and c is original concentration of A^+ ions.

KOHLRAUSCH'S LAW

It states that the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.

$$\lambda = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cations.

ABSOLUTE IONIC MOBILITIES

The absolute ionic mobility of an ion is the velocity of an ion in centimeters per second under a potential gradient of one volt per centimeter. It has been found that the ionic conductance is directly proportional to the ionic mobility *i.e.*

$$\lambda_a = k\,U_a \qquad \text{and} \qquad \lambda_c = k\,U_c$$

where K is the constant of proportionality.

DEGREE OF DISSOCIATION

The degree of dissociation, α, of an electrolyte at the dilution V is given by

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A solution containing 0.00739 g of $AgNO_3$ per gram of water was electrolysed between silver electrodes. During the experiment 0.0078 g of silver was deposited in a silver coulometer placed in series. At the end of experiment, the anodic solution contained 23.14 g of water and 0.236 g of $AgNO_3$. What are the transport numbers of Ag^+ and NO_3^- ions ?

SOLUTION : (i) To calculate the transport number of Ag^+

Before Electrolysis :	After Electrolysis
Mass of water = 1 g	Mass of water = 23.14 g
Mass of $AgNO_3$ = 0.00739 g	Mass of $AgNO_3$ = 0.236 g

No. of gram eqvt. of Ag $= \dfrac{0.00739}{170}$

$= 4.347 \times 10^{-5}$

No. of g equivalents of Ag in 1 g of water

$$= \frac{0.236}{23.14} \times \frac{1}{170}$$

$$= 5.992 \times 10^{-5}$$

Increase in concentration of Ag^+ in the anodic compartment when no silver ions migrate

$$= \frac{0.0078}{170}$$

$$= 4.588 \times 10^{-5}$$

Increase in concentration of Ag^+ ions in the anodic compartment when Ag^+ ions migrate

= Conc. of Ag after electrolysis – Conc. of Ag before electrolysis

$= 5.992 \times 10^{-5} - 4.347 \times 10^{-5}$

$= 1.645 \times 10^{-5}$

Fall in conc. of Ag^+ in anodic compartment $= 4.588 \times 10^{-5} - 1.645 \times 10^{-5}$

$= 2.943 \times 10^{-5}$

$$\textit{Transport number of } Ag^+ \textit{ ions} = \frac{\textit{Fall in conc. around anode}}{\textit{Silver deposited on Ag electrode}}$$

$$= \frac{2.943 \times 10^{-5}}{4.588 \times 10^{-5}}$$

$$= \mathbf{0.641}$$

(ii) To calculate the transport number of NO_3^- ions

$$= 1 - t_{Ag^+}$$

$$= 1 - 0.641$$

$$= \mathbf{0.359}$$

SOLVED PROBLEM 2. The specific conductivity of saturated solution of silver chloride at 18 °C is 1.24×10^{-6} mhos after subtracting that of water. The mobilities of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively. Calculate the solubility of silver chloride in grams per litre.

SOLUTION : (i) To calculate the volume of solution that contain 1 g equivalent of AgCl.

Formula used

$$\lambda = \kappa \times V$$

Quantities given

$\kappa = 1.24 \times 10^{-6}$ mhos $\qquad \lambda = \lambda_{Ag^+} + \lambda_{Cl^+} = 53.8 + 65.3 = 119.1$

Substitution of values

$$119.1 = 1.24 \times 10^{-6} \times V$$

or

$$V = \frac{119.1}{1.24 \times 10^{-6}}$$

$$= 9.6048 \times 10^{7} \text{ ml}$$

(ii) To calculate the solubility of AgCl in gram per litre

$$9.6048 \times 10^{7} \text{ ml contain AgCl} = 1 \text{ g eqvt} = 143.5 \text{ g}$$

$$1000 \text{ ml contain AgCl} = \frac{143.5 \times 1000}{9.604 \times 10^{7}}$$

$$= \mathbf{1.494 \times 10^{-3}}$$

SOLVED PROBLEM 3. In a moving boundary experiment 0.01 N HCl solution was floated on a lithium chloride solution. The tube used had a diameter of 1 cm. When a current of 11.0 milliampere was passed for 20 minutes, the H^+ ions – Li^+ ions boundary moved through 13.9 cm. Calculate the transport numbers of H^+ and Cl^- ions in HCl solution used.

SOLUTION : (i) To calculate the transport no. of H^+

Formula used

$$t_{H^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$s = \pi r^2 = \frac{22}{7} \times 0.5 \times 0.5$ $\qquad l = 13.9$ cm

$F = 96500$ coulomb $\qquad c = 0.01$ N $\qquad Q = 11 \times 10^{-3} \times 20 \times 60$

Substitution of values

$$t_{H^+} = \frac{22}{7} \times \frac{0.5 \times 0.5 \times 13.9 \times 96500 \times 0.01}{11 \times 10^{-3} \times 20 \times 60}$$

$$= \mathbf{0.7984}$$

(ii) To calculate the transport no. of Cl^-.

Formula used

$$t_{Cl^-} = 1 - t_{H^+}$$

Quantities given

$$t_{H^+} = 0.7984$$

Substitution of values

$$t_{Cl^-} = 1 - 0.7984 = \mathbf{0.2016}$$

SOLVED PROBLEM 4. Calculate the equivalent conductivity at 20 °C of NH_4OH at infinite dilution. Given: $\lambda_o(NH_4Cl) = 130$, $\lambda_o(OH^-) = 174$ and $\lambda_o(Cl^-) = 66$.

SOLUTION :

Formula used

$$\lambda_o(NH_4OH) = \lambda_o(NH_4Cl) + \lambda_o(OH^-) - \lambda_o(Cl^-)$$

Quantities given

$\lambda_o(NH_4Cl) = 130$ $\lambda_o(OH^-) = 174$ $\lambda_o(Cl^-) = 66$

Substitution of values

$$\lambda_o(NH_4OH) = 130 + 174 - 66 = \mathbf{238}$$

SOLVED PROBLEM 5. The absolute velocity of Ag^+ is 0.00057 cm sec^{-1} and that of NO_3^- is 0.00069 cm sec^{-1}. Assuming complete dissociation, calculate the specific conductivity of 0.01 M solution of silver nitrate.

SOLUTION :

Formula used

$$\kappa V = \lambda_\infty = \lambda_{Ag^+} + \lambda_{NO_3^-}$$

Quantities given

$\lambda_{Ag^+} = 0.00057 \times 96500$ $\lambda_{NO_3^-} = 0.00069 \times 96500$

$$V = \frac{1000}{0.01}$$

Substitution of values

$$\kappa = \frac{96500(0.00057 + 0.00069) \times 0.01}{1000} \text{ mhos} = \mathbf{0.00121\ mhos}$$

SOLVED PROBLEM 6. The speed ratio of silver and nitrate ions in $AgNO_3$ electrolysed between silver electrodes was found to be 0.89. Calculate the transference number of silver and nitrate ions.

SOLUTION : (i) To calculate the transference no. of NO_3^- ions.

Formula used

$$t_- = \frac{1}{1 + r}$$

Quantities given

$r = 0.89$

Substitution of values

$$t_- = \frac{1}{1 + 0.89} = \frac{1}{1.89} = \mathbf{0.5291}$$

(ii) To calculate the transference number of Ag$^+$ ions.

Formula used

$$\begin{aligned} t_{Ag^+} &= 1 - t_{NO_3^-} \\ &= 1 - 0.5291 \\ &= \mathbf{0.4709} \end{aligned}$$

SOLVED PROBLEM 7. In a moving boundary experiment with 0.1 N KCl using 0.65 N LiCl as indicator solution, a constant current of 0.006 amp was passed for 1900 secs and the boundary was observed to move through 5 cm in a tube of 0.1142 cm^2 cross-section. Calculate the transport number of K$^+$ and Cl$^-$ ions.

SOLUTION : (i) To calculate the transport number of K$^+$ ions.

Formula used

$$t_{K^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$s = 0.1142 \text{ cm}^2$ $\quad l = 5 \text{ cm}$ $\quad F = 96500$ coulomb

$c = 0.1$ $\quad Q = 0.006 \times 1900$ coulomb

Substitution of values

$$\begin{aligned} t_{K^+} &= \frac{0.1142 \times 5 \times 96500 \times 0.1}{1000 \times 0.006 \times 1900} \\ &= \mathbf{0.4833} \end{aligned}$$

(ii) To calculate the transport number of Cl$^-$ ions

Formula used

$$t_{Cl^-} = 1 - t_{K^+}$$

Quantities given

$$t_{K^+} = 0.4833$$

Substitution of values

$$\begin{aligned} t_{Cl^-} &= 1 - 0.4833 \\ &= \mathbf{0.5167} \end{aligned}$$

SOLVED PROBLEM 8. A dilute solution of silver nitrate was electrolysed using platinum electrodes. After passing small current for three hours, a fall of 0.00064 g equivalent of electrolyte occurred in the anionic solution. The weight of copper deposited was found to be 0.05088 gm. Calculate the transport number of silver ions.

SOLUTION :

Formula used

$$\text{Transport No. of Ag}^+ \text{ ions} = \frac{\textit{Fall in concentration}}{\textit{Amt. of Cu deposited in g eqvt}}$$

Quantities given

$$\textit{Fall in Concentration} = 0.00064 \text{ g eqvt.}$$

$$\textit{Amt. of Cu deposited in g eqvt} = \frac{0.05088}{31.5}$$

Substitution of values

$$\begin{aligned} \text{Transport No. of Ag}^+ \text{ ions} &= \frac{0.00064 \times 31.5}{0.05088} \\ &= \mathbf{0.40} \end{aligned}$$

SOLVED PROBLEM 9. A solution of $AgNO_3$ containing 0.5066 g of the salt in 60 g of solution was electrolysed between silver electrodes. After electrolysis 50 g of the anode solution found to contain 0.5186 g of $AgNO_3$ when a current of one ampere was passed for 118 seconds. Calculate the transport numbers of Ag^+ and NO_3^- ions.

SOLUTION : (i) To calculate the transport number of Ag^+ ions.

After electrolysis

Weight of anodic solution taken = 50 g

Weight of $AgNO_3$ present in it = 0.5186 g

Weight of water = 49.4814 g

Before Electrolysis

Weight of $AgNO_3$ solution = 60 g

Weight of $AgNO_3$ present = 0.5066

Weight of water = 59.4934 g

Weight of $AgNO_3$ present in 49.4814g

$$\text{of water} = \frac{0.5066}{59.4934} \times 49.4814$$

$$= 0.421 \text{ g}$$

Observed increase in the weight of $AgNO_3$ in anodic compartment due to electrolysis

$$= 0.5186 - 0.421 \text{ g}$$

$$= 0.0976 \text{ g}$$

$$= \frac{0.0976}{170} \text{ g equiv of } AgNO_3$$

$$= 5.741 \times 10^{-4} \text{ g}$$

$$\text{Quantity of electricity passed} = I \times t$$

$$= 1 \text{ amp} \times 118 \text{ sec}$$

$$= 118 \text{ coulombs}$$

Amount of $AgNO_3$ liberated when 118 coulombs of electricity are passed $= \dfrac{118}{96500}$

$$= 1.223 \times 10^{-3} \text{ g}$$

Loss around the anode due to migration of ions

$$= 1.223 \times 10^{-3} - 5.741 \times 10^{-4}$$

$$= 6.489 \times 10^{-4}$$

$$\text{Transport number of } Ag^+ \text{ ions} = \frac{6.489 \times 10^{-4}}{1.223 \times 10^{-3} \text{ g}}$$

$$= \mathbf{0.530}$$

(ii) To calculate the transport number of NO_3^- ions

$$\text{Transport number of } NO_3^- \text{ ions} = 1 - \text{transport number of } Ag^+$$

$$= 1 - 0.530$$

$$= \mathbf{0.470}$$

SOLVED PROBLEM 10. The equivalent conductance at infinite dilution (Λ_o) of HCl, CH_3COONa and NaCl are 426.16, 91.0 and 126.45 ohm^{-1} cm^2 g equiv^{-1} respectively. Calculate Λ_o of acetic acid.

SOLUTION :

Formula used

$$\Lambda_o (CH_3COOH) = \Lambda_o (CH_3COONa) + \Lambda_o (HCl) - \Lambda_o (NaCl)$$

Quantities given

$\Lambda_o (CH_3COONa) = 91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1}$ $\Lambda_o (NaCl) = 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1}$

$\Lambda_o (HCl) = 426.16 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1}$

Substitution of values

$$\Lambda_o(\text{CH}_3\text{COOH}) = 91.0 + 426.16 - 126.45 \text{ ohm}^{-1}\text{ cm}^2\text{ g equiv}^{-1}$$
$$= \mathbf{390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1}}$$

SOLVED PROBLEM 11. The specific conductance of a saturated solution of AgCl is 1.55×10^{-6} ohm^{-1}cm^{-1} at 25 °C. The ion conductance of Ag^+ and Cl^- are 61.94 and 76.34 ohm^{-1} cm^2 respectively. Calculate the solubility of AgCl in gram equivalent per litre at 25 °C. Neglect the specific conductance of water.

SOLUTION :

Formula used

$$\mu = \frac{\kappa \times 1000}{s}$$

Quantities given

$\mu = \mu_{Ag^+} + \mu_{NO_3^-} = 61.94 + 76.34 = 138.28 \text{ ohm}^{-1}\text{ cm}^2$ $\qquad \kappa = 1.55 \times 10^{-6}$ ohm cm^{-1}

Substitution of values

$$138.28 \text{ ohm}^{-1}\text{ cm}^{-1} = \frac{1.55 \times 10^{-6} \times 1000}{s}$$

or
$$s = \frac{1.55 \times 10^{-6} \times 1000}{138.28}$$
$$= \mathbf{1.1209 \times 10^{-5} \text{ mol lit}^{-1}}$$

SOLVED PROBLEM 12. In a moving boundary experiment with 0.1 N KCl solution, the boundary moved 4.94 cm during 67 minutes when a current of 5.21 A was used. The cross-sectional area of the tube was 0.230 cm^2. Calculate the transport number of K^+ ions.

SOLUTION :

Formula used

$$t_{K^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$s = 0.230$ cm^2 $\qquad l = 4.94$ cm $\qquad F = 96500$ coulomb

$c = 0.1$ N $\qquad Q = 5.21 \times 67 \times 60$ coulombs

Substitution of values

$$t_{K^+} = \frac{0.230 \times 4.94 \times 96500 \times 0.1}{5.21 \times 67 \times 60}$$
$$= \mathbf{0.523}$$

SOLVED PROBLEM 13. Molar conductances of NaOH, NaCl and NH_4Cl are 248.61, 126.45 and 149.75 Ω^{-1} m^2 mol^{-1}. Calculate the molar conductance of NH_4OH.

SOLUTION :

Formula used

$$\mu_{(\text{NH}_4\text{OH})} = \mu_{(\text{NaOH})} + \mu_{(\text{NH}_4\text{Cl})} - \mu_{(\text{NaCl})}$$

Quantities given

$\mu_{(\text{NaOH})} = 248.61\ \Omega^{-1}\text{ m}^2\text{ mol}^{-1}$ $\qquad \mu_{(\text{NH}_4\text{Cl})} = 149.75\ \Omega^{-1}\text{ m}^2\text{ mol}^{-1}$

$\mu_{(\text{NaCl})} = 126.45\ \Omega^{-1}\text{ m}^2\text{ mol}^{-1}$

Substitution of values

$$\mu_{(\text{NH}_4\text{OH})} = 248.61 + 149.75 - 126.45\ \Omega^{-1}\text{ m}^2\text{ mol}^{-1}$$
$$= \mathbf{271.91\ \Omega^{-1}\text{ m}^2\text{ mol}^{-1}}$$

SOLVED PROBLEM 14. In a particular experiment on KCl the apparatus consisted of a tube of diameter 4.176 mm and it contained an aqueous solution of KCl at a concentration of 0.021 mol lit^{-1}. A steady current of 1.82 mA was passed and the cationic boundary advanced 3.18 mm in 100 sec. Find transport number of K$^+$ and Cl$^-$.

SOLUTION : (i) To calculate the transport number of K$^+$

Formula used

$$t_{K^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$$s = \frac{22}{7} \times \frac{0.4176}{2} \times \frac{0.4176}{2}\ \text{cm}^2 \qquad l = 3.18\ \text{mm} = 0.318\ \text{cm}$$

$Q = 1.82 \times 10^{-3} \times 100$ coulomb

$F = 96500$ coulomb $\qquad c = 0.021$ mol lit^{-1}

Substitution of values

$$t_{K^+} = \frac{22}{7} \times \frac{0.4176}{2} \times \frac{0.4176}{2} \times \frac{0.318 \times 96500 \times 0.021}{1.82 \times 10^{-3} \times 100}$$

$$= \mathbf{0.4847}$$

(ii) To calculate the transport number of Cl$^-$

Formula used

$$t_{Cl^-} = 1 - t_{K^+}$$

Quantities given

$$t_{K^+} = 0.4847$$

Substitution of values

$$t_{Cl^-} = 1 - 0.4847$$

$$= \mathbf{0.5153}$$

SOLVED PROBLEM 15. A 0.05 M NaOH solution offered a resistance of 31.6 ohm in a conductivity cell at 298 K. If the cell constant of the cell is 0.367 cm^{-1} find out the molar conductivity of sodium hydroxide solution.

SOLUTION : (i) To calculate the specific conductivity of NaOH solution

Formula used

$$\textit{Specific conductivity, } \kappa = \frac{\textit{Cell constant}}{\textit{Resistance}}$$

Quantities given

Cell constant = 0.367 cm^{-1} $\qquad$ *Resistance* = 31.6 ohm

Substitution of values

$$\text{Specific conductivity, } \kappa = \frac{0.367\ \text{cm}^{-1}}{31.6\ \text{ohm}}$$

$$= 0.0116\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

(ii) To calculate the molar conductivity of NaOH solution

Formula used

$$\Lambda_m = \frac{1000 \times \kappa}{c}$$

Quantities given

$\kappa = 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1}$ $c = 0.05 \text{ M}$

Substitution of values

$$\Lambda_m = \frac{1000 \times 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1}}{0.05 \text{ M}}$$

$$= \mathbf{232.278 \text{ ohm}^{-1} \text{ cm}^{-1}}$$

SOLVED PROBLEM 16. The resistance of 0.1 M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1 M KCl is $1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of a 0.1 M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1 M NaCl solution.

SOLUTION : (i) To calculate the cell constant

Formula used

$$\kappa = \frac{1}{R} \times \textit{cell constant}$$

Quantities given

$\kappa = 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ $R = 300 \text{ ohm}$

Substitution of values

$$1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} = \frac{1}{300 \text{ ohm}} \times \text{cell constant}$$

$$\text{cell constant} = 300 \text{ ohm} \times 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$= 3.87 \text{ cm}^{-1}$$

(ii) To calculate the equivalent conductance of 0.1 M NaCl solution

Formula used

$$\Lambda = \kappa \times \frac{1000}{N}$$

Quantities given

$\kappa = \frac{1}{R} \times \textit{cell constant} = \frac{1}{380} \times 3.87 = 0.01018 \text{ ohm}^{-1} \text{ cm}^{-1}$ $N = 0.1$

Substitution of values

$$\Lambda = \frac{0.01018 \times 1000}{0.1} \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$$

$$= \mathbf{101.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}}$$

SOLVED PROBLEM 17. A solution of silver nitrate containing 6.07 g silver in 25 ml solution was electrolysed between platinum electrodes. After electrolysis, 5.77 g of silver was present in 25 ml of anode solution while 0.625 g of metallic silver was deposited on the cathode. Calculate the transport number of Ag^+ and NO_3^- ions.

SOLUTION : (i) To calculate the transport no. of Ag^+ ions

Formula used

$$\textit{Transport number of } Ag^+ \textit{ ions} = \frac{\textit{Fall in conc. around anode}}{\textit{No. of g eqvt deposited in silver coulometer}}$$

Quantities given

$$\textit{Fall in conc. around anode} = 6.07 - 5.77 \text{ g} = 0.3 \text{ g} = \frac{0.3}{108} \text{ g eqvt.} = 0.002777 \text{ g eqvt.}$$

$$\textit{No. of eqvt. deposited in silver coulometer} = \frac{0.625}{108} = 0.005787 \text{ g eqvt.}$$

Substitution of values

$$\text{Transport number of Ag}^+ \text{ ions} = \frac{0.002777}{0.005787}$$

$$= 0.4799$$

(ii) To calculate the transport number of NO_3^- ions.

$$\text{Transport number of } NO_3^- \text{ ions} = 1 - \text{ transport no. of Ag}^+ \text{ ions}$$

$$= 1 - 0.479$$

$$= \mathbf{0.529}$$

SOLVED PROBLEM 18. Ratio of Ag^+ and NO_3^- ions in the solution of $AgNO_3$ electrolysed between silver electrodes is 0.75. Find the transport number of the two ions.

SOLUTION :

Formula used

$$t_{NO_3^-} = \frac{\mu_{NO_3^-}}{\mu_{NO_3^-} + \mu_{Ag+}}$$

Quantity given

$$\frac{\mu_{Ag^+}}{\mu_{NO_3^-}} = 0.75 \quad \text{or} \quad 1 + \frac{\mu_{Ag^+}}{\mu_{NO_3^-}} = 1.75$$

Substitution of values

$$t_{NO_3^-} = \frac{1}{1.75} = \mathbf{0.571}$$

$$t_{Ag^+} = 1 - t_{NO_3^-}$$

$$= 1 - 0.571$$

$$= \mathbf{0.429}$$

SOLVED PROBLEM 19. In a moving boundary method, a current of 25 mA was passed for 80 seconds. During this time the boundary of a solution of HCl containing 0.01 mol dm^{-3} moved 16.8 cm towards the cathode. Calculate the transport number of H^+ and Cl^- ions. The cross-sectional area of the glass tube is 1.00×10^{-5} m^2.

SOLUTION :

Formula used

$$t_{H^+} = \frac{s \times l \times c}{n}$$

Quantities given

$l = 16.8 \text{ cm} = 16.8 \times 10^{-2} \text{ m}$

$s = 1.0 \times 10^{-5} \text{ m}^2$

$c = 0.01 \text{ mol dm}^{-3}$

$n = \dfrac{Q}{F} = \dfrac{25 \times 10^{-3} \times 80}{96500}$

Substitution of values

$$t_{H^+} = \frac{16.8 \times 10^{-2} \text{ m} \times 1.0 \times 10^{-5} \text{ m}^2 \times 0.01 \text{ mol dm}^{-3}}{\dfrac{25 \times 10^{-3} \times 80}{96500} \times 1000}$$

$$= \mathbf{0.81}$$

and

$$t_{Cl^-} = 1 - t_{H^+}$$

$$= 1 - 0.81$$

$$= \mathbf{0.19}$$

ADDITIONAL PRACTICE PROBLEMS

1. A solution of HCl was electrolysed in a transference cell, between two platinum electrodes. The electrode compartment contained 0.354 g of chloride ions before electrolysis and 0.326 g after electrolysis. A silver coulometer in series had a deposit of 0.532 g of silver after passing the same amount of current. Calculate the transport number of H^+ and Cl^- ions.

Answer. 0.16 and 0.84

2. In an electrolysis of copper sulphate between copper electrodes, the total mass of copper deposited at the cathode was 0.153 g and masses of copper per unit volume of the anode liquid after and before electrolysis are 0.91 and 0.79 g respectively. Calculate the transport number of Cu^{2+} and SO_4^{2-} ions.

Answer. 0.215 and 0.785

3. In the Hittorf cell using silver electrodes and $AgNO_3$ as an electrolyte, a certain amount of current was passing which deposited 9.886×10^{-4} g equivalent of silver in the coulometer. The anode compartment had the composition 28.235 g of H_2O and 0.099 g of $AgNO_3$ before electrolysis and 28.435 g of water and 0.1874 g of $AgNO_3$ after electrolysis. Calculate the transport number of Ag^+ and NO_3^- ions.

Answer. 0.48 and 0.52

4. The ionic conductances of Li^+, Na^+ and K^+ are 38.6, 50.1 and 73.5 ohm^{-1} cm^2 $eqvt^{-1}$ respectively. Calculate ionic mobilities.

Answer. 4×10^{-4}, 5.2×10^{-4} and 7.6×10^{-4}

5. The equivalent conductivity of KCl at infinite dilution is 120 ohm^{-1} cm^2 $eqvt^{-1}$. The transport number of Cl^- ion in KCl at the same temperature is 0.51. Calculate the limiting ionic mobility and ionic conductance of K^+ ions.

Answer. 58.8 ohm^{-1} cm^2 $eqvt^{-1}$, 6.09×10^{-4} cm^2 s^{-1} v^{-1}

6. A conductivity cell whose cell constant is 2 cm^{-1}, is filled with 0.1 M acetic acid solution. Its resistance is found to be 3765 ohm^{-1}. Calculate the degree of dissociation of acetic acid.

Answer. 0.0136

7. A solution of HCl was electrolysed in a cell between two platinum electrodes. The cathode compartment contained 0.354 g of chloride ions before electrolysis and 0.32 g after electrolysis. A silver coulometer in series had a deposit of 0.532 g of silver after passing the same amount of current. Calculate the transport number of H^+ and Cl^- ions.

Answer. 0.84 ; 0.160

8. In a moving boundary method, a current of 30 m A was passed for 80 seconds. During this time the boundary of a solution of HCl containing 0.01 mol dm^{-3} moved 17.0 cm towards the cathode. Calculate the transport number of H^+ and Cl^- ions. (The cross-sectional area of the glass tube is 1.0×10^{-5} m^2).

Answer. 0.68 ; 0.32

9. The ionic equivalent conductances of Na^+ and Cl^- ions in 0.1 molar sodium chloride are 45 and 63 ohm^{-1} cm^2 mol^{-1}. What are their ionic mobilities and transport numbers ?

Answer. 4.66×10^{-4} and 6.53×10^{-4} , 0.417 and 0.583

10. In a moving boundary experiment with 1 N KCl solution using $CaCl_2$ as indicator, a current of 0.0115 A was passed for half an hour and the boundary moved through a volume of 0.106 ml. Calculate the transport number of K^+ ion.

Answer. 0.494

26

Ionic Equilibria
Solubility Product

CHAPTER

KEY CONCEPTS AND EQUATIONS

THE OSTWALD'S DILUTION LAW

The law of Mass action can also be applied to the ionic equilibrium

$$AB \rightleftharpoons A^+ + B^-$$

The Dissociation constant or Ionisation constant for such an equilibrium is given by

$$K_c = \frac{\alpha^2 c}{(1-\alpha)}$$

where α is the degree of dissociation and c is the concentration of the electrolyte. The above expression can also be written as

$$K_c = \frac{\alpha^2}{(1-\alpha)V}$$

where V is volume of solution in litres containing 1 mole of an electrolyte. This expression is called Ostwald's Dilution Law. It reduces to

$$K_c = \frac{\alpha^2}{V}$$

for weak electrolytes when $1-\alpha \cong 1$.

DEGREE OF DISSOCIATION

The fraction of the amount of the electrolyte in solution present as free ions is called the degree of dissociation. It is given by

$$x = \frac{\textit{Amount dissociated}\ (\text{mol lit}^{-1})}{\textit{Initial concentration}\ (\text{mol lit}^{-1})}$$

COMMON ION EFFECT

The reduction of the degree of dissociation of a salt by the addition of a common ion is called the common-ion effect.

SOLUBILITY EQUILIBRIA AND THE SOLUBILITY PRODUCT

A saturated solution is a solution in which the dissolved and undissolved solute are in equilibrium and the solubility of a substance in a solvent is the concentration in the saturated solution.

The molar solubility is defined as the number of moles of the substance per litre of solution.

For the equilibrium

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

we have

$$K = \frac{[Ag^+]\ [Cl^-]}{[AgCl]}$$

In the saturated solution $[AgCl]$ does not change with time and the equilibrium expression becomes

$$K_{sp} = [Ag^+]\ [Cl^-]$$

where K_{sp} is called the solubility product and the product $[Ag^+]$ $[Cl^-]$ is called Ionic product.

CALCULATION OF K_{sp} FROM SOLUBILITY AND VICE VERSA

The K_{sp} expressions for various sparingly soluble salts are given in Table 26.1

TABLE 26.1 K_{sp} EXPRESSIONS FOR VARIOUS SALTS

Salt	Formula	K_{sp}	
Silver Chloride	$AgCl$	$[Ag^+]\ [Cl^-]$	$= s^2$
Barium Fluoride	BaF_2	$[Ba^{2+}]\ [F^-]^2$	$= 4s^3$
Silver Chromate	Ag_2CrO_4	$[Ag^+]^2\ [CrO_4^{2-}]$	$= 4s^3$
Lead sulphate	$PbSO_4$	$[Pb^{2+}]\ [SO_4^{2-}]$	$= s^2$

Knowing the value of K_{sp}, the solubility, s of the salt can be calculated.

PREDICTING WHETHER PRECIPITATION WILL OCCUR ON MIXING

When two reaching solutions are mixed, the ionic product Q is calculated from the concentration of the reacting ions. Following two cases arise

$Q > K_{sp}$ precipitation occurs

$Q < K_{sp}$ No precipitation occurs

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. The solubility product of lead bromide is 8.0×10^{-5}. If the salt is 80% dissociated in the saturated solution, find the solubility of the salt.

SOLUTION :

$$PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^-$$

Formula used

$$K_{sp} = [Pb^{2+}]\ [Br^-]^2$$

Quantity given

$$K_{sp} = 8.0 \times 10^{-5}$$

Substitution of values

$$8.0 \times 10^{-5} = s\,(\text{mol lit}^{-1}) \times [2s\,(\text{mol lit}^{-1})]^2$$

or $$4\,s^3 = 8.0 \times 10^{-5}$$

or $$s = \sqrt[3]{2.0 \times 10^{-5}}$$

$$= 2.714 \times 10^{-2}\ \text{mol lit}^{-1}$$

If the salt is 80% dissociated, the solubility is

$$= \frac{2.714 \times 10^{-2} \times 80}{100} = 2.171 \times 10^{-2} \text{ mol lit}^{-1}$$

$$= 2.17 \times 10^{-2} \times 368 \text{ g lit}^{-1}$$

$$= \mathbf{7.9856 \ g \ lit^{-1}}$$

SOLVED PROBLEM 2. The solubility of silver chloride at 25 °C is 1.05 × 10^{-5} moles per litre. Calculate the solubility product.

SOLUTION :

Formula used

$$K_{sp} = [Ag^+]\ [Cl^-]$$

Quantities given

$[Ag^+] = 1.05 \times 10^{-5}$ mole per litre $\qquad$ $[Cl^-] = 1.05 \times 10^{-5}$ mole per litre

Substitution of values

$$K_{sp} = 1.05 \times 10^{-5} \times 1.05 \times 10^{-5}$$

$$= \mathbf{1.1025 \times 10^{-10}}$$

SOLVED PROBLEM 3. The solubility of $BaSO_4$ at 18 °C is 0.00233 g per litre. Calculate the solubility product of $BaSO_4$. (Molecular weight of $BaSO_4$ is 233)

SOLUTION :

Formula used

$$K_{sp} = [Ba^{2+}]\ [SO_4^{\ 2-}]$$

Quantities given

$$[SO_4^{\ 2-}] = [Ba^{2+}] = 0.00233 \text{ g lit}^{-1} = \frac{0.00233}{233} \text{ mol lit}^{-1} = 1 \times 10^{-3} \text{ mol lit}^{-1}$$

Substitution of values

$$K_{sp} = (1.0 \times 10^{-3}) \times (1.0 \times 10^{-3})$$

$$= \mathbf{1.0 \times 10^{-6}}$$

SOLVED PROBLEM 4. The solubility product of silver chromate is 2.0 × 10^{-12} at 25 °C. Calculate the solubility at this temperature.

SOLUTION :

The equilibrium reaction is

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{\ 2-}$$

Equilibrium concentration $\qquad 2x \qquad x$

Formula used

$$K_{sp} = [Ag^+]^2\ [CrO_4^{\ 2-}]$$

$$= (2x)^2\ (x)$$

$$= 4x^3$$

Quantities given

$$K_{sp} = 2.0 \times 10^{-12}$$

Substitution of values

$$2.0 \times 10^{-12} = 4x^3$$

or

$$x = \sqrt[3]{\frac{2.0 \times 10^{-12}}{4}}$$

$$= \mathbf{7.937 \times 10^{-5} \ mole \ lit^{-1}}$$

SOLVED PROBLEM 5. At 20 °C the solubility of silver chloride in water is 1.435 × 10^{-3} g per litre. Find the solubility of AgCl.

SOLUTION :

$$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+ + Cl^-}$$

Formula used

$$K_{sp} = [Ag^+]\ [Cl^-] = s^2$$

Quantity given

$$s = 1.435 \times 10^{-3}\ \mathrm{g\ lit^{-1}} = \frac{1.435 \times 10^{-3}}{143.5}\ \mathrm{mol\ lit^{-1}}$$
$$= 1 \times 10^{-5}\ \mathrm{mol\ lit^{-1}}$$

Substitution of values

$$K_{sp} = (1 \times 10^{-5}) \times (1 \times 10^{-5})$$
$$= \mathbf{1 \times 10^{-10}}$$

SOLVED PROBLEM 6. The solubility of $\mathrm{Ag_2CrO_4}$ (m. wt = 332) is 0.024 gram $\mathrm{lit^{-1}}$. Find the solubility product.

SOLUTION :

$$\mathrm{Ag_2CrO_4} \rightleftharpoons \mathrm{2Ag^+ + CrO_4^{2-}}$$

Formula used

$$K_{sp} = [Ag^+]^2\ [CrO_4^{2-}]$$
$$= (2s)^2 \times s = 4s^3$$

Quantity given

$$s = 0.024\ \mathrm{g\ lit^{-1}} = \frac{0.024}{332}\ \mathrm{mol\ lit^{-1}} = 7.2289 \times 10^{-5}\ \mathrm{mol\ lit^{-1}}$$

Substitution of value

$$K_{sp} = 4 \times (7.2289 \times 10^{-5})^3$$
$$= \mathbf{1.511 \times 10^{-12}}$$

SOLVED PROBLEM 7. Calculate the pH value of a solution obtained by mixing 500 ml of 0.1 N $\mathrm{CH_3COOH}$ and 500 ml of 0.1 N $\mathrm{CH_3COONa}$. K_a for acetic acid is 1.8 × 10^5.

SOLUTION :

Formula used

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Quantities given

$$pK_a = -\log 1.8 \times 10^5 = 4.774$$

$$[Salt] = \frac{0.1}{2} = 0.05\ \mathrm{N} \qquad [Acid] = \frac{0.1}{2} = 0.05\ \mathrm{N}$$

Substitution of values

$$pH = 4.774 + \log \frac{0.05}{0.05}$$
$$= \mathbf{4.774}$$

SOLVED PROBLEM 8. The dissociation constants for formic acid and acetic acid are 21.4 × 10^{-5} and 1.8 × 10^{-5}respectively. What are the relative strengths of the two acids ?

SOLUTION :

Formula used

$$\frac{\text{Strength of } HCOOH}{\text{Strength of } CH_3COOH} = \sqrt{\frac{K_{HCOOH}}{K_{CH_3COOH}}}$$

Quantities given

$K_1 = 21.4 \times 10^{-5}$ $\qquad$ $K_2 = 1.8 \times 10^{-5}$

Substitution of values

$$\frac{\text{Strength of } HCOOH}{\text{Strength of } CH_3COOH} = \sqrt{\frac{21.4 \times 10^{-5}}{1.8 \times 10^{-5}}}$$

$$= \mathbf{3.448}$$

Thus formic acid is 3.448 times stronger than the acetic acid.

SOLVED PROBLEM 9. Calculate the *pH* value of a solution whose hydrogen ion concentration is 0.006 gm ion/litre.

SOLUTION :

Formula used

$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 0.006 \text{ g lit}^{-1} = \frac{0.006}{2} \text{ mol lit}^{-1} = 0.003 \text{ mol lit}^{-1}$$

Substitution of values

$$\begin{aligned} pH &= -\log (0.003) \\ &= -\log (3 \times 10^{-3}) \\ &= (3 - 0.4771) \\ &= \mathbf{2.5229} \end{aligned}$$

SOLVED PROBLEM 10. What is the *pH* of the buffer composed of 0.1M solution of HCN in 0.1M KCN ? The dissociation constant of HCN is 0.01.

SOLUTION :

Formula used

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Quantities given

$pK_a = -\log K_a = -\log 0.02 = 1.6990$

$[Salt] = 0.1$ M $\qquad$ $[Acid] = 0.1$ M

Substitution of values

$$pH = 1.6990 + \log \frac{0.1}{0.1}$$

$$= \mathbf{1.6990}$$

SOLVED PROBLEM 11. Calculate the *pH* of (i) 10^{-8} N aqueous HCl solution ; and (ii) 10^{-7} N aqueous NaOH solution.

SOLUTION : (i) 10^{-8} N aqueous HCl solution

Formula used

$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 10^{-8}$$

Substitution of values

$$pH = -\log(10^{-8})$$
$$= \mathbf{8}$$

(ii) 10^{-7} N aqueous NaOH solution

Formula used

$$pH = -\log[H^+]$$

Quantity given

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-7}} = 10^{-7}$$

Substitution of values

$$pH = -\log(10^{-7})$$
$$= \mathbf{7}$$

SOLVED PROBLEM 12. The solubility of Ag_2CrO_4 (mol. mass = 332) is 0.024 g lit^{-1}. Find the solubility product.

SOLUTION : The solubility equilibrium is

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^-$$

Equilibrium Conc. $\quad s \quad 2s \quad s$

$$\text{Solubility of } Ag_2CrO_4 = 0.024 \text{ g lit}^{-1}$$
$$= \frac{0.024}{332} \text{ mol lit}^{-1}$$
$$= 7.229 \times 10^{-5} \text{ mol lit}^{-1}$$
$$\text{Solubility product of } Ag_2CrO_4 = [Ag^+]^2\ [CrO_4^{2-}]$$
$$= (2 \times 7.229 \times 10^{-5}) \times 7.229 \times 10^{-5}$$
$$= \mathbf{1.052 \times 10^{-12}}$$

SOLVED PROBLEM 13. The specific conductivity of a saturated solution of silver chloride is 1.33×10^{-6} mhos at 25 °C. Given that the ionic conductivities for Ag^+ and Cl^- ions are 56.9 and 68.4 mhos respectively. Calculate the solubility and solubility product of silver chloride.

SOLUTION : To calculate the solubility of AgCl.

Formula used

$$\lambda_\infty = \kappa \times V$$

Quantities given

$$\lambda_\infty = \Lambda_{Ag+} + \Lambda_{Cl^-} = 56.9 + 68.4 = 125.3 \qquad \kappa = 1.33 \times 10^{-6}$$

Substitution of values

$$125.3 = 1.33 \times 10^{-6} \times V$$

or
$$V = \frac{125.3}{1.33 \times 10^{-6}} = 94.2 \times 10^6 \text{ cm}^3$$
$$94.2 \times 10^6 \text{ cm}^3 \text{ contain AgCl} = 1 \text{ g equivalent} = 143.5 \text{ g AgCl}$$
$$1000 \text{ cm}^3 \text{ contain AgCl} = \frac{143.5 \times 1000}{94.2 \times 10^{-6}}$$
$$= \mathbf{1.523 \times 10^{-3} \text{ g lit}^{-1}}$$

(ii) To calculate the solubility product of AgCl

Formula used

$$K_{sp} = [Ag^+]\ [Cl^-]$$

Quantities given

$$[Ag^+] = [Cl^-] = \frac{1.523 \times 10^{-3}\ \text{g lit}^{-1}}{143.5\ \text{g lit}^{-1}} = 1.06 \times 10^{-5}\ \text{mol lit}^{-1}$$

Substitution of values

$$\begin{aligned} K_{sp} &= (1.06 \times 10^{-5})\ (1.06 \times 10^{-5}) \\ &= \mathbf{1.1236 \times 10^{-10}} \end{aligned}$$

SOLVED PROBLEM 14. The solubility product of Ag_2CrO_4 at 25 °C is 1.29 × 10^{-11} mol lit^{-3}. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 ml water is shaken with excess of Ag_2CO_3 till the following equilibrium is reached :

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_2$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3.

SOLUTION :

$$Ag_2C_2O_4 \rightleftharpoons 2Ag^+ + C_2O_4^{2-}$$

$$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$$

$$K_{sp}\ (Ag_2C_2O_4) = [Ag^+]^2\ [C_2O_4^{2-}]$$

or

$$[Ag^+]^2 = \frac{K_{sp}[Ag_2C_2O_4]}{[C_2O_4^{2-}]} \qquad \text{...(i)}$$

and

$$K_{sp}\ (Ag_2CO_3) = [Ag^+]^2\ [CO_3^{2-}]$$

or

$$[Ag^+]^2 = \frac{K_{sp}[Ag_2CO_3]}{[CO_3^{2-}]} \qquad \text{...(ii)}$$

Since the concentration $[Ag^+]$ is the same in equations (i) and (ii) we have

$$\frac{K_{sp}[Ag_2C_2O_4]}{[C_2O_4^{2-}]} = \frac{K_{sp}[Ag_2CO_3]}{[CO_3^{2-}]} \qquad \text{... (iii)}$$

The chemical reaction between Ag_2CO_3 and $K_2C_2O_4$ is

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

	$K_2C_2O_4$	K_2CO_3
Initial Conc.	0.152	0
Conc. at Equilibrium	0.152 – 0.0358	0.0358
equilibrium conc. (mol lit^{-1})	0.2324	0.0716

Substituting the values in equation (iii) we have

$$\begin{aligned} K_{sp}\ [Ag_2CO_3] &= \frac{K_{sp}[Ag_2C_2O_4] \times [C_2O_4^{2-}]}{[CO_3^{2-}]} \\ &= \frac{1.29 \times 10^{-11}\ \text{mol}^3\ \text{lit}^{-3} \times 0.0716\ \text{mol lit}^{-1}}{0.2324\ \text{mol lit}^{-1}} \\ &= \mathbf{3.97 \times 10^{-12}\ mol^3\ lit^{-3}} \end{aligned}$$

SOLVED PROBLEM 15. The solubility product K_{sp} of $Ca(OH)_2$ at 2.98 K is 4.42×10^{-5}. 500 ml of a saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligram is precipitated ?

SOLUTION : The ionisation of $Ca(OH)_2$ is represented as

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$\begin{aligned} K_{sp} \text{ of } Ca(OH)_2 &= [Ca^{2+}]\,[OH^-]^2 \\ &= s \times (2s)^2 \\ &= 4s^3 \end{aligned}$$

or
$$\begin{aligned} s &= \sqrt[3]{\frac{K_{sp}}{4}} \\ &= \sqrt[3]{\frac{4.42 \times 10^{-5}}{4}} \\ &= 2.227 \times 10^{-2}\ \text{M} \end{aligned}$$

$$\begin{aligned} \text{No. of moles of } Ca^{2+} \text{ ions in 500 ml of the solution } &= \frac{2.227 \times 10^{-2}}{2} \\ &= 0.011135 \end{aligned}$$

When 500 ml of saturated solution is mixed with 500 ml of 0.4 M NaOH the resultant volume is 1000 ml. The molarity of OH^- ions in the resultant solution becomes 0.2 M

Now
$$\begin{aligned} [Ca^{2+}] &= \frac{K_{sp}}{[OH^-]^2} \\ &= \frac{4.42 \times 10^{-5}}{0.2 \times 0.2} \\ &= 0.001105\ \text{M} \end{aligned}$$

No. of moles of Ca^{2+} ions or $Ca(OH)_2$ precipitated

$$\begin{aligned} &= \text{Initial conc. of } Ca^{2+} - \text{Final conc. of } Ca^{2+} \\ &= 0.011135 - 0.001105 \\ &= 0.010245\ \text{M} \end{aligned}$$

$$\begin{aligned} \text{Thus the mass of } Ca(OH)_2 \text{ precipitated } &= 0.010245 \times 74 \\ &= 0.75813\ \text{g} \\ &= \mathbf{758.13\ mg} \end{aligned}$$

SOLVED PROBLEM 16. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^-, with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water ? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions ? (Assume $CaCO_3$ to be completely insoluble in water). If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its *pH* ?

SOLUTION : The reactions are

$$CaO + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + H_2O$$

or
$$\underset{40\text{ g}}{Ca^{2+}} + \underset{122\text{ g}}{2HCO_3^-} \longrightarrow CaCO_3 + H_2O + CO_2$$

122 g of HCO_3^- ions are precipitated by = 40 g of Ca^{2+} ions

∴ 183 g of HCO_3^- ions are precipitated by $= \frac{40 \times 183}{122}$ g of Ca^{2+} ions

= 60 g of Ca^{2+} ions

But 40 g of Ca^{2+} ions are present in = 56 g of CaO

and 60 g of Ca^{2+} ions are present in $= \frac{56 \times 60}{40}$ g of CaO

= 84 g of CaO

No. of moles of CaO in 84 g of CaO $= \frac{84 \text{ g}}{56 \text{ g mol}^{-1}} = 1.5$ mol

96 ppm of SO_4^{2-} = 96 ppm of Ca^{2+} ions

∴ Conc. of $CaSO_4$ = 96 ppm

$= \frac{96}{136}$

= 0.706 mol of $CaSO_4$

= **0.706×10^{-3} mol lit^{-1}**

∴ when 0.706×10^{-3} mol in 1 litre Ca^{2+} ions exchanged with H^+ ions of water

Concentration of H^+ ions $= 2 \times 0.706 \times 10^{-3}$ mol lit^{-1}

$= 1.412 \times 10^{-3}$ mol lit^{-1}

or Concentration of OH^+ ions $= 1.412 \times 10^{-3}$ mol lit^{-1}

$pOH = -\log [OH^-]$

$= -\log (1.412 \times 10^{-3})$

$= 2.85$

$pH = 14 - pOH = 14 - 2.85$

= **11.15**

SOLVED PROBLEM 17. The solubility of a salt of type AB_2 with mol mass 78 in water is 1.6×10^{-2} g lit^{-1} at 20 °C. Calculate its solubility product.

SOLUTION : The equilibrium is

$$AB_2 \rightleftharpoons A^{2+} + 2B^-$$

The solubility of the salt AB_2 in moles per litre

$$= \frac{1.6 \times 10^{-2} \text{ g lit}^{-1}}{78 \text{ g mol}^{-1}}$$

$= 2.05 \times 10^{-4}$ mol lit^{-1}

Formula used

$$K_{sp} = [A^{2+}]\ [B^-]^2$$

Quantities given

$[A^{2+}] = 2.05 \times 10^{-4}$ mol lit^{-1}

$[B^-] = 2 \times 2.05 \times 10^{-4}$ mol lit^{-1}

$= 4.1 \times 10^{-4}$ mol lit^{-1}

Substitution of values

$$K_{sp} = 2.05 \times 10^{-4} \times (4.1 \times 10^{-4})^2$$

= **3.446×10^{-11}**

ADDITIONAL PRACTICE PROBLEMS

1. A sample of hard water contains 0.005 mole of $CaCO_3$ per litre. What is the minimum concentration of Na_2SO_4 which must be exceeded for removing the calcium ions from this water sample? The solubility product constant of calcium sulphate at 25 °C is 2.40×10^{-5}.

Answer. greater than 0.0048 mol lit^{-1}

2. When one litre of saturated solution of lead chloride, $PbCl_2$ is evaporated to dryness, the residue is found to weight 4.5 g. Calculate the value of K_{sp} for $PbCl_2$.

Answer. 1.7×10^{-5}

3. Calculate the solubility product of AgCl if its solubility at 20 °C is 1.435×10^{-5} g/litre.

Answer. 1×10^{-10}

4. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g lit^{-1}. Calculate its solubility (g lit^{-1}) in 0.02 M $Mg(OH)_2$ solution

Answer. 8.7×10^{-4} g lit^{-1}

5. Calculate the solubility product of $AgCl_{(s)}$ in pure water and in 0.1 M NaCl at 25 °C.

K_{sp} (AgCl) = 2.8×10^{-10}

Answer. 1.673×10^{-5} mol lit^{-1} ; 2.8×10^{-9} mol lit^{-1}

6. The solubility product of AgCl in water is 1.5×10^{-10}. Calculate its solubility in 0.01 M NaCl solution.

Answer. 1.5×10^{-8} mol lit^{-1}

7. Calculate the solubility product of silver chromate (molar mass 332) if at 25 °C it requires 0.0435 g of Ag_2CrO_4 to form its one litre saturated solution.

Answer. 5.24×10^{-12}

8. Calculate the solubility product of silver chromate Ag_2CrO_4 at 25 °C if the concentration of Ag^+ ion 1.5×10^{-4} mol lit^{-1} is in a saturated solution of silver chromate at 25 °C.

Answer. $K_{sp} = 1.6875 \times 10^{-12}$

9. The solubility of lead sulphate in water 0.038 g lit^{-1} at 25 °C. Calculate its solubility product at 25 °C.

(molar mass of $PbSO_4$ = 303).

Answer. 1.5725×10^{-8}

10. The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find out the solubility in pure water and in 0.1 M $BaCl_2$ solution.

Answer. 3.87×10^{-5} mol lit^{-1} ; 1.5×10^{-8} mol lit^{-1}

27

Acids and Bases

CHAPTER

KEY CONCEPTS AND EQUATIONS

ARRHENIUS CONCEPTS

An acid is a compound that releases H^+ ions in water ; and a base in a compound that releases OH^- ions in water.

BRONSTED LOWRY CONCEPT

An acid is any molecule or ion that can donate a proton (H^+) and a base is any molecule or ion that can accept a proton.

LEWIS CONCEPT

An acid is a substance which accepts an electron pair and a base is a substance that donates an electron pair.

RELATIVE STRENGTH OF ACIDS AND BASES

The dissociation constant of an acid, HA, is given by

$$K_a = \frac{[H^+]\,[A^-]}{[HA]}$$

The value of K_a is a measure of $[H^+]$ or its acid strength.

The dissociation constant of a base, BOH, is given by

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]}$$

The value of K_b is a measure of $[OH^-]$ or its strength.

THE pH OF SOLUTIONS

The *pH* is defined as the negative of logarithm of H^+ ion concentration. Mathematically,

$$pH = -\log\,[H^+]$$

Similarly for a base *pOH* is defined as the negative of logarithm of OH^- ion concentration. i.e.,

$$pOH = -\log\,[OH^-]$$

And for water

$$pK_w = -\log\,[K_w]$$

The pK_w is related to *pH* and *pOH* by the relation

$$pK_w = pH + pOH$$

BUFFER SOLUTION

A buffer solution is one which maintains its *pH* fairly even upon the addition of small amounts of acid or base. In other words, a buffer solution resists a change in its *pH* on the addition of a small amount of an acid or base.

The *pH* of a buffer solution is given by

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

or

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Two hypothetical acids HA and HB have the dissociation constant 1×10^{-3} and 1×10^{-5} respectively in water at 25 °C. Calculate the strength of HA with respect to HB.

SOLUTION :

Formula used

$$\frac{Strength\ of\ acid\ HA}{Strength\ of\ acid\ HB} = \sqrt{\frac{K_{HA}}{K_{HB}}}$$

Quantities given

$K_{HA} = 1 \times 10^{-3}$ $\qquad$ $K_{HB} = 1 \times 10^{-5}$

Substitution of values

$$\frac{Strength\ of\ acid\ HA}{Strength\ of\ acid\ HB} = \sqrt{\frac{1 \times 10^{-3}}{1 \times 10^{-5}}}$$

$$= \sqrt{1 \times 10^{2}}$$

$$= \mathbf{10}$$

Thus, acid HA is 10 times stronger than HB.

SOLVED PROBLEM 2. Dissociation constant of propionic acid at 25 °C is 1.34×10^{-5}. Calculate the degree of dissociation and *pH* in 0.1 M acid.

SOLUTION : (i) To calculate the degree of dissociation of propionic acid

Formula used

$$K_a = \frac{\alpha^2 C}{1-\alpha} \quad \text{or} \quad \alpha^2 C \qquad [\because 1-\alpha \approx 1]$$

Quantities given

$K_a = 1.34 \times 10^{-5}$ $\qquad$ $C = 0.1$ M

Substitution of values

$$1.34 \times 10^{-5} = \alpha^2 \times 0.1$$

or

$$\alpha^2 = \frac{1.34 \times 10^{-5}}{0.1}$$

or

$$\alpha = \sqrt{1.34 \times 10^{-4}}$$

$$= 0.0115$$

(ii) To calculate the pH of 0.1 M propionic acid

Formula used

$$pH = -\log[H^+]$$

Quantities given

$$[H^+] = 0.0115 \text{ M}$$

Substitution of value

$$\begin{aligned} pH &= -\log(0.0115) \\ &= \mathbf{1.939} \end{aligned}$$

SOLVED PROBLEM 3. Calculate the *pH* of 0.001 N HCl assuming complete ionisation of HCl.

SOLUTION :

$$\underset{0.001 \text{ M}}{\text{HCl}} \rightleftharpoons \underset{0.001 \text{ M}}{\text{H}^+} + \text{Cl}^-$$

Formula used

$$pH = -\log[H^+]$$

Quantities given

$$[H^+] = 0.001 \text{ N}$$

Substitution of value

$$\begin{aligned} pH &= -\log(0.001) \\ &= \mathbf{3} \end{aligned}$$

SOLVED PROBLEM 4. Given the dissociation constant of acetic acid at 25 °C as 1.8×10^{-5}, calculate the *pH* of a solution containing 0.185 mol acetic acid and 3.015 g mol sodium acetate per litre.

SOLUTION :

Formula used

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Quantities given

$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447$ $[Salt] = 3.015 \text{ M}$ $[Acid] = 0.185 \text{ M}$

Substitution of values

$$\begin{aligned} pH &= 4.7447 + \log \frac{3.015}{0.185} \\ &= 4.7447 + \log 16.297 \\ &= 4.7447 + 1.2121 \\ &= \mathbf{5.9568} \end{aligned}$$

SOLVED PROBLEM 5. Calculate *pH* of 0.085 N monobasic acid which dissociates 25%.

SOLUTION : (i) To calculate the concentration of [H$^+$] ions.

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$$

Since the acid is 25% dissociated, the concentration of H$^+$ will be

$$\begin{aligned} [H^+] &= \frac{25}{100} \times 0.085 \text{ M} \\ [H^+] &= 0.02125 \text{ M} \end{aligned}$$

(ii) To calculate the pH value

Formula used

$$pH = -\log[H^+]$$

Quantity given

$$[H^+] = 0.02125 \text{ M}$$

Substitution of values

$$pH = -\log(0.02125)$$
$$= \mathbf{1.6726}$$

SOLVED PROBLEM 6. Calculate the pH of a 0.1 M acetic acid when it is half neutralised by NaOH solution ($K_a = 1.7 \times 10^{-5}$).

SOLUTION : Acetic acid dissociates as

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Let x be the concentration of H^+ ions at equilibrium, then

$$[H^+] = [CH_3COO^-] = x$$
$$[CH_3COOH] = 0.05 - x \cong 0.05$$

Substituting the values we get

$$K_a = \frac{x \times x}{0.05}$$

Quantity given

$$K_a = 1.7 \times 10^{-5}$$

Substitution of values

$$1.7 \times 10^{-5} = \frac{x^2}{0.05}$$

or $$x^2 = 8.5 \times 10^{-7}$$

or $$x = 9.219 \times 10^{-4}$$

Now $$pH = -\log[H^+]$$
$$= -\log(9.219 \times 10^{-4})$$
$$= \mathbf{3.0353}$$

SOLVED PROBLEM 7. Calculate the pH of the buffer solution containing 0.04 M NH_4Cl and 0.02 M NH_4OH. K_b for NH_4OH is 1.8×10^{-5}.

SOLUTION :

Formula used

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

Quantities given

$pK_b = -\log\ 1.8 \times 10^{-5} = 4.7447$ $[Salt] = 0.04$ M $[Base] = 0.02$ M

Substitution of values

$$pOH = 4.7447 + \log\frac{0.04}{0.02}$$
$$= 4.7447 + \log 2$$
$$= 4.7447 + 0.3010$$
$$= 5.0457$$

Since $$pH + pOH = 14$$
$$pH = 14 - pOH$$
$$= 14 - 5.0457$$
$$= \mathbf{8.9543}$$

SOLVED PROBLEM 8. A buffer solution is prepared by mixing 3 g of acetic acid and 1.30 g of sodium acetate ($CH_3COONa.3H_2O$) and making the total volume to one litre. Calculate the *pH* of the buffer. ($K_a = 1.8 \times 10^{-5}$; $H = 1$; $C = 12$; $O = 16$; $Na = 23$)

SOLUTION :

Formula used

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Quantities given

$$pK_a = -\log K_a = -\log (1.8 \times 10^{-5}) = 4.7447$$

$$[Salt] = \frac{1.30}{136} = 9.559 \times 10^{-3}\,\text{M} \qquad [Acid] = \frac{3}{60} = 0.05\,\text{M}$$

Substitution of values

$$\begin{aligned} pH &= 4.7447 + \log \frac{9.559 \times 10^{-3}}{0.05} \\ &= 4.7447 - 0.7185 \\ &= \mathbf{4.0262} \end{aligned}$$

SOLVED PROBLEM 9. Calculate the degree of hydrolysis of ammonium acetate. The dissociation constant of NH_4OH is 1.8×10^{-5} and that of acetic acid is 1.8×10^{-5} and $K_w = 1.0 \times 10^{-14}$.

SOLUTION :

Formula used

$$K_h = \frac{K_w}{K_a\ K_b}$$

Quanities given

$$K_w = 1 \times 10^{-14} \qquad K_a = 1.8 \times 10^{-5} \qquad K_b = 1.8 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}} \\ &= \mathbf{3.0864 \times 10^{-5}} \end{aligned}$$

SOLVED PROBLEM 10. Calculate the *pH* of solution having hydrogen ion concentration 2.5×10^{-3} M.

Solution :

Formula used

$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 2.5 \times 10^{-3}\,\text{M}$$

Substitution of values

$$\begin{aligned} pH &= -\log (2.5 \times 10^{-3}) \\ &= -\log (0.0025) \\ &= -(-2.6020) \\ &= \mathbf{2.6020} \end{aligned}$$

SOLVED PROBLEM 11. Calculate the *pH* of 0.01 M NH_4OH solution. Dissociation constant of NH_4OH is 1.8×10^{-5}.

SOLUTION : **(i) To calculate the concentration of OH^- ions.**

$$\underset{0.01 - \alpha}{NH_4OH} \rightleftharpoons \underset{\alpha}{NH_4^+} + \underset{\alpha}{OH^-}$$

Formula used

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]}$$

$$= \frac{\alpha^2}{0.01-\alpha}$$

$$= \frac{\alpha^2}{0.01} \qquad [\because 0.01-\alpha \approx 0.01]$$

or $$\alpha = \sqrt{0.01 \times K_b}$$

Substitution of values

$$\alpha = \sqrt{0.01 \times 1.8 \times 10^{-5}}$$

or $$\alpha = \sqrt{1.8 \times 10^{-7}}$$

$$[OH^-] = \alpha = 4.2426 \times 10^{-4}$$

(ii) To calculate pOH value

Formula used

$$pOH = -\log [OH^-]$$

Quantity given

$$[OH^-] = 4.2426 \times 10^{-4}$$

Substitution of value

$$pH = 14 - pOH$$

$$= 14 - 3.3723$$

$$= \mathbf{10.6277}$$

SOLVED PROBLEM 12. Calculate the pH of 0.001 M HCl and 0.01 M NaOH.

SOLUTION : (i) To calculate the pH of 0.001 M HCl

$$\underset{0.001\ M}{HCl} \rightleftharpoons \underset{0.001M}{H^+ + Cl^-}$$

Formula used

$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 0.001\ M$$

Substitution of value

$$pH = -\log (0.001)$$

$$= \mathbf{3}$$

(ii) To calculate pH of 0.01 M NaOH

$$\underset{0.01\ M}{NaOH} \rightleftharpoons \underset{0.01M}{Na^+ + OH^-}$$

Formula used

$$pOH = -\log [OH^-]$$

Quantity given

$$[OH^-] = 0.01\ M$$

Substitution of value

$$pOH = -\log 0.01 = 2$$

Since

$$pH + pOH = 14$$

we have

$$pH = 14 - pOH$$
$$= 14 - 2$$
$$= \mathbf{12}$$

SOLVED PROBLEM 13. Calculate the *pH* volume of a solution obtained by mixing 0.083 mole of acetic acid and 0.091 mole of sodium acetate and making the volume 500 ml. K_a for acetic acid is 1.75×10^{-5}.

SOLUTION :

Formula used

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Quantities given

$pK_{a,} = -\log 1.75 \times 10^{-5} = 4.7569$ $\quad$ $[Salt] = 2 \times 0.091 \text{ M} = 0.182$

$[Acid] = 2 \times 0.083 \text{ M} = 0.166$

Substitution of values

$$pH = 4.7569 + \log \frac{0.182}{0.166}$$
$$= 4.7569 + \log 1.0964$$
$$= 4.7569 + 0.0399$$
$$= \mathbf{4.7968}$$

SOLVED PROBLEM 14. What will be the H^+ ion concentration of solutions having (i) $pH = 5.0$ and (ii) $pH = 7.8$?

SOLUTION :(i) To calculate the $[H^+]$ of solution having pH = 5

Formula used

$$pH = -\log [H^+]$$

or

$$[H^+] = \text{Antilog } (-pH)$$

Quantity given

$$pH = 5$$

Substitution of value

$$[H^+] = \text{Antilog } (-5)$$
$$= \mathbf{1 \times 10^{-5} \text{ M}}$$

(ii) To calculate the $[H^+]$ of solution having pH = 7.8

Formula used

$$pH = -\log [H^+]$$

or

$$[H^+] = \text{Antilog } (-pH)$$

Quantity given

$$pH = 7.8$$

Substitution of value

$$[H^+] = \text{Antilog } -7.8$$
$$= \mathbf{1.584 \times 10^{-8}}$$

SOLVED PROBLEM 15. What is pH of the solution when 0.20 mole of HCl is mixed to one litre of a solution containing

(i) 1 M each of acetic acid and acetate ion.

(ii) 0.1 M each acetic acid and acetate ion.

SOLUTION : (i) When 1 M each of acetic acid and acetate ion are mixed

$$[CH_3COOH] = [CH_3COONa] = 1\,M \qquad \text{(Given)}$$

$$\text{Amount of HCl added} = 0.20\text{ mole}$$

$$\underset{0.2\,M}{HCl} \rightleftharpoons \underset{0.2\,M}{H^+ + Cl^-}$$

H^+ ions combine with acetate ions to give acetic acid *i.e.*

$$\underset{0.2\,M}{H^+} + \underset{0.2\,M}{CH_3COO^-} \longrightarrow \underset{0.2\,M}{CH_3COOH}$$

The concentration of CH_3COOH will increase and it becames 1.2 M and that of CH_3COO^- decreases to 0.8 M

Formula used

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

Quantities given

$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447$ $[Salt] = 0.8\,M$ $[Acid] = 1.2\,M$

Substitution of values

$$pH = 4.7447 + \log\frac{0.8}{1.2}$$
$$= 4.7447 + \log 0.667$$
$$= 4.7447 + (-0.1759)$$
$$= \mathbf{4.5688}$$

(ii) When 0.1 M each of acetic acid and acetate ion are mixed

$$[CH_3COOH] = [CH_3COONa] = 0.1\,M$$

Out of 0.2 M HCl added 0.1 M will react with acetic ion to form 0.1 M of acetic acid. Thus the concentration of CH_3COOH would increase to 0.1 M + 0.1 M = 0.2 M

And in the presence of H^+, the concentration of CH_3COOH does not increase. Thus pH of the solution will be due to the presence of H^+ ions of HCl *i.e.*

$$[H^+] = 0.2\,M - 0.1\,M = 0.1\,M$$
$$pH = -\log[H^+]$$
$$= -\log(0.1)$$
$$= \mathbf{1}$$

SOLVED PROBLEM 16. How many moles of HCl will be required to prepare one litre of a buffer solution containing NaCN and HCl of pH 8.5 using 0.01 gram formula weight of NaCN ?

K (dissociation constant) of HCN = 4.1×10^{-1}

SOLUTION : The required pH = 8.5

$$pH = -\log[H^+]$$

$$\therefore \qquad [H^+] = \text{Antilog}\,(-8.5)$$
$$= 3.16 \times 10^{-9}\,\text{M}.$$

This buffer solution can be prepared by mixing CN^- with HCN in proper proportions.

$$HCN \rightleftharpoons H^+ + CN^-$$
$$K_w = \frac{[H^+]\,[CN^-]}{[HCN]}$$

or
$$\frac{[CN^-]}{[HCN]} = \frac{K_w}{[H^+]} = \frac{4.1 \times 10^{-10}}{3.16 \times 10^{-9}} = 0.1294$$

The ratio of $[CN^-]$ to [HCN] can be obtained by mixing a suitable amount of HCl which neutralise a part of weak base CN^-. Let concentration of [HCN] be '*a*' *i.e.*

$$[CN^-] = 0.01 - a$$

Then
$$\frac{[CN^-]}{[HCN]} = \frac{0.01 - a}{a} = 0.1294$$

or
$$a = 9.87 \times 10^{-3}\,\text{M}$$

Thus
$$[HCN] = 9.87 \times 10^{-3}\,\text{M}$$

and
$$[CN^-] = 0.01 - 9.87 \times 10^{-3}\,\text{M}$$
$$= \mathbf{1.277 \times 10^{-4}\,M}$$

Thus buffer can be prepared by mixing 0.01 mole of NaCN and 9.87×10^{-3} M HCl in one litre of water.

SOLVED PROBLEM 17. Freshly prepared Aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol lit^{-1} of ammonium chloride and 0.05 mole lit^{-1} of ammonium hydroxide. Calculate the concentration of Al^{3+} and Mg^{2+} ions in the solution.

$$K_b\,(NH_4OH) = 1.8 \times 10^{-5}$$
$$K_{sp}\,Mg\,(OH)_2 = 6.0 \times 10^{-10}$$
$$K_{sp}\,Al\,(OH)_3 = 6.0 \times 10^{-32}$$

SOLUTION : (i) To calculate pOH value

Formula used

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Quantities given

$pK_b = -\log(1.8 \times 10^{-5}) = 4.7447$ $\qquad$ $[Salt] = 0.25$ M $\qquad$ $[Base] = 0.05$ M

Substitution of values

$$pOH = 4.7447 + \log \frac{0.25}{0.05}$$
$$= 4.7447 + \log 5$$
$$= 4.7447 + 0.6990$$
$$= 5.4437$$

(ii) To calculate the concentration of OH^- ions.

$$pOH = -\log[OH^-]$$
$$5.4437 = -\log[OH^-]$$
$$[OH^-] = \text{Antilog}\,(-5.4437)$$
$$= 3.6 \times 10^{-6}$$

(iii) To calculate the concentration of Al^{3+} and Mg^{2+} ions.

$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$$

$$K_{sp}[Al(OH)_3] = [Al^{3+}][OH^-]^3 = 6.0 \times 10^{-32}$$

or
$$[Al^{3+}] = \frac{K_{sp}[Al(OH)_3]}{[OH^-]^3} = \frac{6.0 \times 10^{-32}}{(3.6 \times 10^{-6})^3}$$
$$= \mathbf{1.286 \times 10^{-15}\ M}$$

Also
$$K_{sp}[Mg(OH)_2] = [Mg^{2+}][OH^-]^2 = 6.0 \times 10^{-10}$$

or
$$[Mg^{2+}] = \frac{K_{sp}[Mg(OH)_2]}{[OH^-]^2}$$
$$= \frac{6.0 \times 10^{-10}}{(3.6 \times 10^{-6})^2}$$
$$= 4.63 \times 10$$
$$= \mathbf{46.3}$$

SOLVED PROBLEM 18. What is the pH of 1.0 M solution of acetic acid ? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value ? (Given $K_a = 1.8 \times 10^{-5}$)

SOLUTION : (i) To calculate the pH of 1.0 M solution of acetic acid

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{[H^+]^2}{[CH_3COOH]} \qquad \because [CH_3COOH] = [H^+]$$

$$[H^+]^2 = K_a \times [CH_3COOH]$$

$$[H^+]^2 = 1.8 \times 10^{-5} \times 1.0$$

or
$$H^+ = \sqrt{1.8 \times 10^{-5} \times 1.0}$$
$$= 4.24 \times 10^{-3}\ M$$

Now
$$pH = -\log[H^+]$$
$$= -\log(4.24 \times 10^{-3})$$
$$= 2.3726$$

(ii) To calculate the volume of the solution

$$\text{pH of the diluted solution} = 2 \times 2.3726$$
$$= 4.7452$$

$$pH = -\log[H^+] = 4.7452 = -\log\sqrt{K_a'}$$

or
$$-1/2 \log K_a' = 4.7452$$

or
$$\log K_a' = -9.4904$$

or
$$K_a' = \text{Antilog}(-9.4904)$$
$$= 3.233 \times 10^{-10}$$

$$\text{Concentration of diluted } CH_3COOH = \frac{K_a'}{K_a}$$

$$[CH_3COOH]_{Dil.} = \frac{3.233 \times 10^{-10}}{1.8 \times 10^{-5}} = 1.7961 \times 10^{-5}\ M$$

Let V be the volume of the diluted solution.

Applying $$M_1 V_1 = M_2 V_2$$

$$1 \times 1 = 1.7961 \times 10^{-5} \times V$$

or $$V = \frac{1}{1.7961 \times 10^{-5}} \text{ lit}$$

$$= \mathbf{5.567 \times 10^4 \text{ lit}}$$

SOLVED PROBLEM 20. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagent is 0.6 mol lit^{-1}. (pK_b for $NH_3 = 4.7$) Also take log 2 = 0.3.

SOLUTION :

Formula used

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Quantities given

$pOH = 14 - pH = 14 - 9.0 = 5.0$ $\qquad pK_b = 4.7$

Substitution of values

$$5 = 4.7 + \log \frac{[Salt]}{[Base]}$$

or $$\log \frac{[Salt]}{[Base]} = 0.3$$

$$= \log 2$$

or $$\frac{[Salt]}{[Base]} = 2$$

Let the amount of NH_4Cl be x mol lit^{-1}. Then

$$\frac{x}{0.6 - x} = 2$$

or $$x = 1.2 - 2x$$

or $$3x = 1.2$$

$$= 0.4 \text{ mol lit}^{-1}$$

Thus the amount of NH_4Cl = **0.4 mol lit^{-1}**

and the amount of NH_3 = 0.6 – 0.4 = **0.2 mol lit^{-1}**

ADDITIONAL PRACTICE PROBLEMS

1. The dissociation constant of a base at 25 ºC is 1.5×10^{-10}. Calculate the concentration of hydroxyl ions in 0.015 M solution. Also calculate its degree of dissociation.

Answer. 1.5×10^{-6} ; 0.0001

2. Calculate the *pH* of the following solution :

(i) 0.0002 M HCl

(ii) 0.1 M NH_4OH $(K_b = 1.8 \times 10^{-5})$

Answer. (i) 3.6990 ; (ii) 11.13

3. Calculate the hydrogen ion concentration in a sample of blood having *pH* = 7.4.

Answer. 3.98×10^{-8} M

4. The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10}.

Answer. $[H^+] = 7.2 \times 10^{-10}$ M **;** $[OH^{-1}] = 1.4 \times 10^{-5}$ M

5. Calculate the change in *pH* of 1 litre of buffer solution containing 0.10 mole of each NH_3 and NH_4Cl upon addtion of

(i) 0.02 mole of dissolved gaseous HCl

(ii) 0.02 mole of dissloved NaOH.

Assuming no change in solution volume K_b of $NH_3 = 1.8 \times 10^{-5}$

Answer. (i) 0.176 unit decrease (ii) 0.176 unit increase

6. A 40.0 ml solution of a weak base, B OH, is treated with 0.1 N HCl solution . The *pH* values of the solution are found to be 10.04 and 9.14 after the addition of 5.0 ml and 20.0 ml of the acid respectively. Find out the dissociation constant of the base.

Answer. 1.82×10^{-5}

7. What is the pH of 0.50 M aqueous NaCN solution ? pK_b of CN^- is 4.70`

Answer. 11.5

8. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M ?

(K_a for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$)

Answer. 1×10^{-2}

9. K_a for ascorbic acid (H Asc) is 5×10^{-5}. Calculate the hydrogen ion concentration is an aqueous solution in which the concentration of A Sc^- ions is 0.20 M.

Answer. 5×10^{-9} M

10. Calculate the *pH* of a solution made by mixing 50 ml of 0.01 M $Ba(OH)_2$ solution with 50 ml of water.

Answer. 12

28

Salt Hydrolysis

CHAPTER

KEY CONCEPTS AND EQUATIONS

HYDROLYSIS

The reaction of anion or cation with water accompanied by cleavage of O – H bond is called hydrolysis. In anionic hydrolysis the solution becomes slightly basic due to the generation of excess OH^- ions. In cationic hydrolysis there is excess of H^+ ions which make the solution slightly acidic.

Anionic Hydrolysis $A^- + H-O-H \rightleftharpoons HA + OH^-$ (Basic Solution)

Cationic Hydrolysis $B^+ + H-O-H \rightleftharpoons BOH + H^+$ (Acidic Solution)

Different salts on hydrolysis give acidic, basic or neutral solution depending upon their nature. Their hydrolysis behavior is summarised in Table 28.1.

TABLE 28.1 HYDROLYTIC BEHAVIOUR OF DIFFERENT TYPE OF SALTS

Type of Salt	Examples	Resulting solution
Salt of weak acid & strong base	CH_3COOH, NaCN, etc.	Basic
Salt of weak base & strong acid	NH_4Cl, $AlCl_3$, $FeCl_3$, $CuSO_4$	Acidic
Salt of weak acid & weak base	NH_4OOCH_3, NH_4CN, NH_4F	Basic or Acidic or neutral
Salt of strong acid & strong base	NaCl, KNO_3, Na_2SO_2, etc.	Neutral

HYDROLYSIS CONSTANT

The hydrolysis constant, K_h, of salt of a weak acid and strong base is given by

$$K_h = \frac{[HA][OH^-]}{[A^-]}$$

RELATION BETWEEN K_H, K_W AND K_A

$$\frac{K_w}{K_a} = K_h$$

From the relation it is clear that weaker the acid greater is the hydrolysis constant of the salt.

RELATION BETWEEN HYDROLYSIS CONSTANT AND DEGREE OF HYDROLYSIS

The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is represented by α and is given by

$$\alpha = \sqrt{\frac{K_w}{K_a C}}$$

To calculate pH value of an aqueous solution of weak acid and strong base.

The formula used is

$$pH = ½\, p\, K_w + ½\, pK_a + ½ \log C$$

Salt of weak base and strong acid

The hydrolysis constant of a salt of weak base and strong acid is given by

$$K_h = \frac{[H^+]\,[BOH]}{[B^+]}$$

Relation between K_h, K_w and K_b

$$\frac{K_w}{K_b} = K_h$$

The hydrolysis constant K_h varies inversely as the dissociation constant, K_b, of the base.

Relation between hydrolysis constant and degree of hydrolysis

$$\alpha = \sqrt{\frac{K_w}{K_h \times C}}$$

The *pH* is given by

$$pH = ½\, p\, K_w - ½ \log C + ½\, p\, K_b$$

The value of *pH* will always be less then 7. Thus the solution of a salt of weak base and strong acid will always be acidic.

Salt of weak acid and weak base

The hydrolysis constant is given by

$$K_h = \frac{K_w}{K_a \times K_b}$$

and the degree of hydrolysis is given by

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

The *pH* of the solution is given by

$$pH = ½\, p\, K_w + ½\, p\, K_a - ½\, p\, K_b$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the *pH* of 0.05 N sodium benzoate solution. K_a for $C_6H_5COOH = 6.37 \times 10^{-5}$ and $K_w = 1 \times 10^{-14}$

SOLUTION :

Formula used

$$pH = ½\, pK_w + ½\, pK_a + ½ \log C$$

Quantities given

$pK_w = -\log 10^{-14} = 14$

$C = 0.05$

$pK_a = -\log\, 6.37 \times 10^{-5} = 4.1958$

Substitution of values

$$pH = ½ \times 14 + ½ \times 4.1958 + ½ \ (1.3010)$$

$$= 7 + 2.0979 - 0.6505$$

$$= \mathbf{8.4474}$$

SOLVED PROBLEM 2. Sodium phenate is hydrolysed to the extent of 0.03% in 0.1 M aqueous solution at 25 ºC. Calculate the (i) hydrolysis constant of the salt and (ii) the ionic product of water at 25 ºC. The dissociation constant of phenol is 1.3 x 10^{-10} at 25 ºC.

SOLUTION : (i) To calculate the ionic product of water

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$\alpha = 0.03$ $\quad K_a = 1.3 \text{ x } 10^{-10}$ $\quad C = 0.1$

Substitution of values

$$\frac{K_w}{K_a \times C} = \alpha^2$$

$$K_w = 1.3 \times 10^{-10} \times 0.1 \times (0.03)^2$$

$$= \mathbf{1.17 \times 10^{-14}}$$

(ii) To calculate the hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$K_w = 1.17 \times 10^{-14}$ $\quad K_a = 1.3 \times 10^{-5}$

Substitution of values

$$K_h = \frac{1.17 \times 10^{-14}}{1.3 \times 10^{-5}}$$

$$= 0.9 \times 10^{-9}$$

$$= \mathbf{9 \times 10^{-10}}$$

SOLVED PROBLEM 3. A 0.02 M solution of sodium acetate in water at 25 ºC has a hydrogen concentration of 3×10^{-9} M. What is the hydrolysis constant of the salt ?

SOLUTION : (i) To calculate the K_a of the acid

Formula used

$$[H^+] = \sqrt{\frac{K_w \ K_a}{C}} \quad \text{or} \quad [H^+]^2 = \frac{K_w \ K_a}{C}$$

Quantities given

$[H^+] = 3 \times 10^{-9}$ $\quad K_w = 1 \times 10^{-14}$ $\quad C = 0.02$

Substitution of values

$$(3 \times 10^{-9})^2 = \frac{10^{-14} \times K_a}{0.02}$$

or

$$K_a = \frac{9 \times 10^{-18} \times 0.02}{10^{-14}} = 1.8 \times 10^{-5}$$

(ii) To calculate the hydrolysis constant of sodium acetate.

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$K_w = 10^{-14}$ $\qquad$ $K_a = 1.8 \times 10^{-5}$

Substitution of values

$$K_h = \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$$= \mathbf{5.5 \times 10^{-10}}$$

SOLVED PROBLEM 4. Calculate the pH of a decinormal solution of ammonium chloride. ($pK_a = 5.7$ and $pK_w = 14$).

SOLUTION :

Formula used

$$pH = \tfrac{1}{2} pK_w + \tfrac{1}{2} pK_b - \tfrac{1}{2} \log C$$

Quantities given

$pK_b = 5.7$ $\qquad$ $pK_w = 14$

Substitution of values

$$pH = 7 + \tfrac{1}{2} \times 5.7 - \tfrac{1}{2} \log 0.1$$

$$= 7 + 2.85 - \tfrac{1}{2} (-1)$$

$$= 7 + 2.85 + 0.5$$

$$= \mathbf{10.35}$$

SOLVED PROBLEM 5. The dissociation constant of acetic acid is 1.8×10^{-5} at 18 ºC. The ionic product of water is 10^{-14} at 18 ºC. What would be the degree of hydrolysis in a 0.012 N solution of sodium acetate?

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$K_w = 10^{-14}$ $\qquad$ $K_a = 1.8 \times 10^{-5}$ $\qquad$ $C = 0.012$

Substitution of values

$$\alpha = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.012}}$$

$$= \sqrt{4.623 \times 10^{-9}}$$

$$= \mathbf{6.799 \times 10^{-5}}$$

SOLVED PROBLEM 6. Calculate the degree of hydrolysis of sodium acetate. Dissociation constant of acetic acid is 1.8×10^{-5} and Ionic product of water is 1×10^{-14}

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$K_w = 1 \times 10^{-14}$ $K_a = 1.80 \times 10^{-5}$ $C = 0.1$

Substitution of values

$$\alpha = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}}$$

$$= \sqrt{5.55 \times 10^{-9}}$$

$$= \mathbf{7.45 \times 10^{-5}}$$

SOLVED PROBLEM 7. Calculate the percentage of hydrolysis of sodium acetate in 0.1 N solution at 25 ºC using the following data. It is to be assumed that the salt in completely dissociated.

$K_a = 1.8 \times 10^{-5}$; $K_w = 1.02 \times 10^{-14}$.

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$K_w = 1.02 \times 10^{-14}$ $K_a = 1.8 \times 10^{-5}$ $C = 0.1$

Substitution of values

$$\alpha = \sqrt{\frac{1.02 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}}$$

$$= \mathbf{7.527 \times 10^{-5}}$$

SOLVED PROBLEM 8. The dissociation constant of ammonium hydroxide and hydrocyanic acid are respectively 1.8×10^{-5} and 7.2×10^{-7} and the ionic product of water is 1×10^{-14} Calculate the degree of hydrolysis and hydrolytic constant for ammonium cyanide in 0.01 M solution.

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Quantities given

$K_w = 1 \times 10^{-14}$ $K_a = 1.8 \times 10^{-5}$ $K_b = 7.2 \times 10^{-7}$

Substitution of values

$$\alpha = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 7.2 \times 10^{-7}}}$$

$$= \sqrt{7.716 \times 10^{-4}}$$

$$= \mathbf{2.777 \times 10^{-2}}$$

SOLVED PROBLEM 9. A 0.02 molar solution of sodium acetate in water at 25 ºC is found to have a hydrogen ion concentration of 3.0×10^{-9} gram ion weight per litre. What is the hydrolytic constant of the salt ? ($K_w = 1 \times 10^{-14}$).

SOLUTION :

(i) To calculate the value of Ka

Formula used

$$pH = \tfrac{1}{2} pK_w + \tfrac{1}{2} pK_a + \tfrac{1}{2}\log C$$

Quantities given

$pH = -\log[H^+] = -\log(3\times10^{-9}) = 8.523$ $\qquad C = 0.02\text{M}$

Substitution of values

$$\begin{aligned} 8.523 &= 7 + \tfrac{1}{2} pK_a + \tfrac{1}{2}\log(0.02) \\ &= 7 + \tfrac{1}{2} pK_a + \tfrac{1}{2}(-1.6990) \\ pK_a &= 2\times(8.523 - 7 + 0.8495) \\ &= 4.745 \end{aligned}$$

or
$$\begin{aligned} K_a &= \text{Antilog}(4.745) \\ &= 1.80\times10^{-5} \end{aligned}$$

(ii) To calculate the hydrolysis constant

Formula used

$$K_h = \sqrt{\frac{K_w}{K_a\times C}}$$

Quantities given

$K_w = 1\times10^{-14}$ $\qquad K_a = 1.80\times10^{-5}$ $\qquad C = 0.02$

Substitution of values

$$\begin{aligned} K_h &= \sqrt{\frac{1\times10^{-14}}{1.80\times10^{-5}\times0.02}} \\ &= \sqrt{2.777\times10^{-8}} \\ &= \mathbf{1.666\times10^{-4}} \end{aligned}$$

SOLVED PROBLEM 10. Calculate the hydrolysis constant, degree of hydrolysis and *pH* value of 10^{-2} M NH_4Cl solution at 290 K. ($K_b = 1.8\times10^{-5}$ and $K_w = 1.0\times10^{-14}$).

SOLUTION :(i) To calculate the hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_b}$$

Quantities given

$K_w = 1.0\times10^{-14}$ $\qquad K_b = 1.8\times10^{-5}$

Substitution of values

$$\begin{aligned} K_h &= \frac{1.0\times10^{-14}}{1.8\times10^{-5}} \\ &= \mathbf{5.55\times10^{-10}} \end{aligned}$$

(ii) To calculate the degree of hydrolysis

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_b\times C}}$$

Quantities given

$K_w = 1 \times 10^{-14}$ $\quad$ $K_b = 1.8 \times 10^{-5}$ $\quad$ $C = 10^{-2}$

Substitution of values

$$\alpha = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 10^{-2}}}$$

$$= \sqrt{5.555 \times 10^{-8}}$$

$$= \mathbf{2.357 \times 10^{-4}}$$

(iii) To calculate the pH

$$pH = ½\, pK_w - ½\, pK_b + ½ \log C$$

Quantities given

$pK_w = 14$ $\quad$ $pK_b = -\log 1.8 \times 10^{-5} = 4.7447$ $\quad$ $C = 10^{-2}$

Substitution of values

$$pH = ½ \times 14 - ½\,(4.7447) + ½ \log 10^{-2}$$

$$= 7 - 2.37235 + ½\,(-2)$$

$$= \mathbf{3.62765}$$

SOLVED PROBLEM 11. The hydrogen ion concentration of 0.02 sodium acetate is found to be 3.0×10^{-9} M at 25 °C. Calculate the hydrolysis constant of this salt. $K_w = 1.0 \times 10^{-14}$.

SOLUTION : (i) To calculate K_a of the acid

Formula used

$$pH = ½\, pK_w + ½\, pK_a + ½ \log C$$

Quantities given

$pH = -\log (3.0 \times 10^{-9}) = 8.523$ $\quad$ $pK_w = -\log\,(1 \times 10^{-14}) = 14$ $\quad$ $C = 0.02\text{M} = 10^{-2}\text{M}$

Substitution of values

$$8.523 = ½ \times 14 + ½\, pK_a + ½ \log 10^{-2}$$

$$8.523 = 7 + ½\, pK_a + ½\,(-1.6989)$$

or

$$pK_a = 2 \times (1.523 + 0.84945)$$

$$= 4.7449$$

or

$$K_a = \text{Antilog}\,(-4.7449) = 1.799 \times 10^{-5}$$

(ii) To calculate the hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$K_w = 1.0 \times 10^{-14}$ $\quad$ $K_a = 1.799 \times 10^{-5}$

Substitution of values

$$K_h = \frac{1 \times 10^{-14}}{1.799 \times 10^{-5}}$$

$$= \mathbf{5.55 \times 10^{-10}}$$

SOLVED PROBLEM 12. Calculate the hydrolysis constant and degree of hydrolysis of 0.1M sodium acetate solution. Given : $K_w = 1.0 \times 10^{-14}$ and $K_a = 1.75 \times 10^{-5}$

SOLUTION : (i) To calculate hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$K_w = 1.0 \times 10^{-14}$ $K_a = 1.75 \times 10^{-5}$

Substitution of values

$$K_h = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}}$$

$$= 5.71 \times 10^{-10}$$

(ii) To calculate the hydrolysis constant

Formula used

$$\alpha = \sqrt{\frac{K_h}{C}}$$

Quantities given

$K_h = 5.71 \times 10^{-14}$ $C = 0.1$

Substitution of values

$$\alpha = \sqrt{\frac{5.71 \times 10^{-10}}{0.1}}$$

$$= \mathbf{7.55 \times 10^{-5}}$$

SOLVED PROBLEM 13. Calculate the percentage hydrolysis of sodium acetate in 0.2 M solution at 25 ºC assuming the salt is completely dissociated. K_a for acetic acid = 1.8×10^{-5} and $K_w = 1.0 \times 10^{-14}$.

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$K_w = 1.0 \times 10^{-14}$ $K_a = 1.8 \times 10^{-5}$ $C = 0.2$ M

Substitution of values

$$\alpha = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.2}}$$

$$= \sqrt{2.777 \times 10^{-9}}$$

$$= 5.27 \times 10^{-5}$$

$$\% \text{ Hydrolysis} = 5.27 \times 10^{-5} \times 100$$

$$= \mathbf{5.27 \times 10^{-3}\ \%}$$

SOLVED PROBLEM 14. Calculate the *pH* at the equivalence point when a solution of 0.10M acid is titrated with a solution of 0.10 M sodium hydroxide. K_a for acetic acid = 1.9×10^{-5}.

SOLUTION :

Formula used

$$pH = \tfrac{1}{2}\, pK_w + \tfrac{1}{2}\, pK_a + \tfrac{1}{2}\log C$$

Quantities given

$pK_w = 14$ $\quad pK_a = -\log K_a = \log(1.9 \times 10^{-5}) = 4.7212$ $\quad C = \dfrac{0.1\text{ M}}{2} = 0.05\text{ M}$

Substitution of values

$$\begin{aligned} pH &= \tfrac{1}{2} \times 14 + \tfrac{1}{2} \times 4.7212 + \tfrac{1}{2}\log 0.05 \\ &= 7 + 2.3606 - \frac{1.3010}{2} \\ &= \mathbf{8.7101} \end{aligned}$$

SOLVED PROBLEM 15. Calculate the *pH* and hydrolysis constant of 0.05 M NH_4Cl solution. $K_{NH_4OH} = 1.75 \times 10^{-5}$ and $K_w = 1 \times 10^{-14}$.

SOLUTION : (i) To calculate pH value

Formula used

$$pH = \tfrac{1}{2}\, pK_w - \tfrac{1}{2}\, pK_b - \tfrac{1}{2}\log C$$

Quantities given

$pK_w = -\log K_w = -\log\ 1 \times 10^{-14} = 14$ $\quad pK_b = -\log K_b = -\log 1.75$ $\quad C = 0.05\text{M}$

Substitution of values

$$\begin{aligned} pH &= \tfrac{1}{2} \times 14 - \tfrac{1}{2} \times (4.7569) - \tfrac{1}{2}\log 0.05 \\ &= 7 - 2.37845 - (-1.3010) \\ &= \mathbf{5.92255} \end{aligned}$$

(ii) To calculate the hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_b}$$

Quantities given

$K_w = 1 \times 10^{-14}$ $\quad K_b = 1.75 \times 10^{-5}$

Substitution of values

$$\begin{aligned} K_h &= \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} \\ &= \mathbf{5.714 \times 10^{-10}} \end{aligned}$$

SOLVED PROBLEM 16. Calculate the degree of hydrolysis and *pH* of 0.02M solution of sodium acetate. Hydrolysis constant of sodium acetate is 5.6×10^{-10}.

SOLUTION : (i) To calculate the degree of hydrolysis

Formula used

$$K_a = \sqrt{\frac{K_h}{C}}$$

Quantities given

$K_h = 5.6 \times 10^{-10}$ $\qquad$ $C = 0.02\text{M}$

Substitution of values

$$\alpha = \sqrt{\frac{5.6 \times 10^{-10}}{0.02}}$$

$$= \sqrt{2.8 \times 10^{-8}}$$

$$= \mathbf{1.67 \times 10^{-4}}$$

(ii) To calculate the pH of the solution

Formula used

$$pH = \tfrac{1}{2}\, pK_w + \tfrac{1}{2}\, pK_a + \tfrac{1}{2}\, \log C$$

Quantities given

$pK_w = 14$ $\qquad$ $pK_a = -\log\ K_a = -\log \dfrac{K_w}{K_h} = -\log \dfrac{10^{-14}}{5.6 \times 10^{-10}}$

$\text{C} = 0.02\text{ M}$ $\qquad$ $= -\log 1.786 \times 10^{-5} = +4.7482$

Substitution of values

$$pH = \tfrac{1}{2} \times 14 + \tfrac{1}{2}\ (+4.7482) + \tfrac{1}{2}\ \log (0.02)$$

$$= 7 + 2.3741 + \tfrac{1}{2}\ (-1.6990)$$

$$= 9.3741 - 0.8495$$

$$= \mathbf{8.5246}$$

SOLVED PROBLEM 17. Calcium lactate is a salt of a weak organic acid and represented by Ca $(\text{Lac})_2$. A saturated solution of Ca $(\text{Lac})_2$ contain 0.13 mol of this salt in 0.5 litre solution. The *pOH* of this solution is 5.60. Assuming complete dissociation of the salt, calculate K_a of Lactic acid.

SOLUTION :

The equilibrium reaction is

$$\text{Ca (Lac)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\,\text{Lac}^-$$

	Ca (Lac)_2	Ca^{2+}	$2\,\text{Lac}^-$
Initial conc.	0.13 M × 2	0	0
Equilibrium conc.	0		0.13 M × 2 × 2

Formula used

$$pH = \tfrac{1}{2}\ pK_w + \tfrac{1}{2}\ pK_a + \tfrac{1}{2}\ \log C$$

Quantities given

$pK_w = 14$ $\qquad$ $pH = pK_w - p_{OH} = 14 - 5.60 = 8.4$ $\qquad$ $C = 0.52\text{ M}$

Substitution of values

$$8.40 = \tfrac{1}{2} \times 14 + \tfrac{1}{2}\ pK_a + \tfrac{1}{2}\ \log\ 0.52$$

$$= 7 + \tfrac{1}{2}\ pK_a + \tfrac{1}{2}\ (-0.2840)$$

$$\tfrac{1}{2}\ pK_a = 8.40 - 7 + 0.142$$

$$pK_a = 2 \times 1.542 = 3.084$$

or

$$K_a = \text{Antilog}\ (-3.084)$$

$$= \mathbf{8.24 \times 10^{-4}}$$

SOLVED PROBLEM 18. Calculate the pH of 0.50 M aqueous NaCN solution. pK_b of CN^- is 4.70.

SOLUTION :

Formula used

$$pH = \tfrac{1}{2}\ pK_w + \tfrac{1}{2}\ pK_a + \tfrac{1}{2}\ \log\ C$$

Quantities given

$pK_w = 14$ $\quad pK_a = 14 - pK_b = 14 - 4.70 = 9.30$ $\quad C = 0.50\ \text{M}$

Substitution of values

$$\begin{aligned} pH &= \tfrac{1}{2} \times 14 + \tfrac{1}{2} \times 9.30 + \tfrac{1}{2}\ \log 0.50 \\ &= 7 + 4.65 + \tfrac{1}{2}\ (-0.3010) \\ &= 11.65 - 0.1505 \\ &= \mathbf{11.4995} \end{aligned}$$

SOLVED PROBLEM 19. Calculate the percentage of hydrolysis of 0.003 M aqueous solution of NaOCN.

K_a for HOCN $= 3.33 \times 10^{-4}$

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$K_w = 1 \times 10^{-14}$ $\quad K_a = 3.33 \times 10^{-4}$ $\quad C = 0.003\ \text{M}$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{1 \times 10^{-14}}{3.33 \times 10^{-4} \times 0.003}} \\ &= \sqrt{1.0 \times 10^{-8}} \\ &= 1.0 \times 10^{-4} \\ \%\ \text{age of hydrolysis} &= 1.0 \times 10^{-4} \times 100 \\ &= \mathbf{1.0 \times 10^{-2}} \end{aligned}$$

SOLVED PROBLEM 20. K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in aqueous solution in which the concentration of Asc^- ions is 0.02 M.

SOLUTION : The equilibrium reaction is

	$Asc^- + H_2O$	$HAsc^-$	$+\ OH^-$
Initial Conc.	0.02	0	0
Equilibrium Conc.	$0.02 - x$	x	x

(i) To calculate the concentration of H^+.

Formula used

$$K_h = \frac{[HAsc]\ [OH^-]}{[Asc^-]} = \frac{x^2}{0.02 - x}$$

Quantities given

$$K_h = \frac{K_w}{K_a} = \frac{1\times 10^{-14}}{5\times 10^{-5}} = 2\times 10^{-10}$$

Substitution of values

$$2\times 10^{-10} = \frac{x^2}{0.02} \qquad \text{(neglecting } x \text{ in denominator)}$$

$$x^2 = 2\times 10^{-10}\times 0.02$$

or $$x = \sqrt{4\times 10^{-12}}$$

$$= 2\times 10^{-6}$$

$$[OH^-] = 2\times 10^{-6}$$

and $$[H^+] = \frac{K_w}{2\times 10^{-6}} = \frac{1\times 10^{-14}}{2\times 10^{-6}} = \mathbf{5\times 10^{-9}\,M}$$

(ii) To calculate the degree of hydrolysis

$$\text{Percentage of hydrolysis} = \frac{2\times 10^{-6}}{0.02}\times 100$$

$$= \mathbf{0.01\%}$$

ADDITIONAL PRACTICE PROBLEMS

1. 20 ml of 0.1 M NaOH solution is added to 100 ml of 0.1 M solution of acetic acid calculate the *pH* of the buffer solution (K_a for $CH_3COOH = 1.8\times 10^{-5}$)

Answer. 4.423

2. How many moles of sodium propionate should be added to the litre of an aqueous solution containing 0.02 mole of propionic acid to obtain a buffer of *p*H = 4.75 ? What will be the *pH* if 0.01 mole of HCl is added ?

Answer. 1.52×10^{-2} M ; 4.11

3. 20 ml of 0.2 M NaOH solution be treated with 40 ml of 0.2 M acetic acid solution to give 70 ml. Calculate the *pH* of the solution.

Answer. 4.5684

4. The *pH* of 0.1 M HCN solution is 5.2. Calculate the value of K_a for HCN.

Answer. 39.7×10^{-11}

5. How many gram mole of Cl will be required to prepare one litre of a buffer solution of NaCN and HCN of p*H* 8.5 using 0.01 gm formula weight of NaCN ?

Answer. 0.0089 M

6. What happens to the *pH* of 500 ml of solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 ml of 0.1 M NaOH is added ?

Answer. *pH* will increase

7. Calculate the percent hydrolysis of 0.1 M hydrazine hydrochloride if the basic ionization constant for hydrazine ($NH_2 - NH_2$) is 9.6×10^{-7}.

Answer. 0.032%

8. Calculate the *pH* at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH. K_a for acetic acid is 1.9×10^{-5}.

Answer. 8.71

9. Calculate the hydrolysis constant of sodium acetate and degree of hydrolysis in 0.001M solution. Also calculate its *pH* value. Given K_a for acetic acid = 1.75×10^{-5} and K_w for water = 1×10^{-14}.

Answer. 5.7×10^{-10} ; 7.55×10^{-4} ; 7.88

10. Calculate the hydrolysis of KF. Determine the degree of hydrolysis of salt in 0.01 M solution. Also calculate the *pH* of the solution. K_a (HF) = 1.6×10^{-4}.

Answer. 1.5×10^{-11} ; 3.87×10^{-5} ; 7.59

11. The *pH* of a 0.1 M solution of NH_4Cl is 5.127. Calculate the degree of hydrolysis and hyrolysis constant of NH_4Cl.

Answer. 7.46×10^{-5} ; 5.56×10^{-10}

12. Calculate the percentage hydrolysis of sodium acetate in 0.1 N solution at 298 K, assuming the salt to be completely dissociated. (K_a for Acetic acid = 1.8×10^{-5})

Answer. 0.0075%

13. Calculate the degree of hydrolysis of potassium acetate is 0.1 M solution. Also calculate the *pH* of the solution if K_a for CH_3COOH is 1.8×10^{-5}.

Answer. 7.5×10^{-5} ; 8.88

14. Calculate the degree of hydrolysis of a mixture of aniline and acetic acid in 0.1 M solution.
($K_a = 1.8 \times 10^{-5}$ and $K_b = 4.6 \times 10^{-10}$)

Answer. 0.523

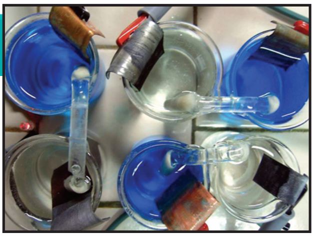
15. The concentration of H^+ ions in a 0.2 M solution of HCOOH is 6.4×10^{-3} mole lit^{-1}. To this solution sodium formate is added so as to adjust the concentration of sodium formate to be 1 mole lit^{-1}. Calculate the *pH* of the solution. K_a for HCOOH = 2.4×10^{-4} and degree of dissociation of HCOONa is 74%.

Answer. 4.18

29

Electromotive Force

CHAPTER



KEY CONCEPTS AND EQUATIONS

REDOX REACTION

A reaction in which loss of electrons (oxidation) and gain of electrons take place simultaneously is called Oxidation-Reduction reaction or Redox reaction. The half reaction that occurs by oxidation is called oxidation half reaction and the second half that occurs by reduction is called reduction half reaction.

ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell. It consists of two half cells joined together with the help of a salt bridge. The emf of a cell is given by

$$\begin{aligned} E_{cell} &= E_{cathode} - E_{anode} \\ &= E_R - E_L \end{aligned}$$

where E_R and E_L are the reduction potentials of right and left cells respectively.

RELATION BETWEEN EMF AND FREE ENERGY

When a cell produces a current, the currents can be used to do work. The maximum amount of work, W_{max}, obtainable from the cell by

$$W_{max} = -\, n\, F\, E$$

where n is the number of electrons transferred and is equal to the valence of the ion participating in the cell reaction, F stands for Faraday and is equal to 96500 coulombs and E is the EMF of the cell.

THE NERNST EQUATION

Nernst derived a mathematical relationship which enables us to calculate the half cell, E from the standard electrode potential, E^o, with the help of the following relation.

$$E = E^o - \frac{2.303\, RT}{nF} \log K$$

where K is the equilibrium constant for the half-cell reaction.

For the reaction

$$M^{n+} + n\,e^- \rightleftharpoons M$$

Nernst equation becomes

$$E = E^o - \frac{2.303\, RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

The concentration of solid metal $[M]$ is equal to zero.

Thus
$$E = E^{o} - \frac{2.303\,RT}{nF} \log [M^{n+}]$$

CONCENTRATION CELL

Cell potential depends on the concentration of the electrolyte. Thus a cell can be constructed by pairing two half cells in which identical electrodes are dipping in solutions of different concentrations of the same electrolyte. Such a cell is called concentration cell.

The emf of a concentration cell is given by

$$E_{cell} = \frac{2.303\,RT}{nF} \log \frac{C_2}{C_1}$$

or
$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

DETERMINATION OF pH

A half cell is set up with the test solution as electrolyte. The emf of the cell depends upon the concentration of H^+ ions or pH of the solution. The emf of the half cell is determined by coupling it with another standard half-cell and measuring the emf of the complete cell. The equations obtained by using different electrodes are as follows :

(i) Using Hydrogen electrode

$$E_{cell} = 0.0591 \times pH \qquad \text{or} \qquad pH = \frac{E_{cell}}{0.0591}$$

(ii) Using Standard calomel

$$E_{cell} = 0.2415 + 0.0591 \times pH \qquad \text{or} \qquad pH = \frac{E_{cell} - 0.245}{0.0591}$$

(iii) Using Quinhydrone electrode

$$E_{cell} = 0.6996 + 0.0591 \times pH - 0.2415 \quad \text{or} \quad pH = \frac{0.4581 - E_{cell}}{0.0591}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the emf of the following cell

$$\text{Sn} \,|\, \text{Sn}^{++},\ 0.75\ \text{N} \,||\, \text{Sn}^{++},\ 0.5\ \text{N} \,|\, \text{Sn}$$

SOLUTION :

Formula used

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Quantities given

$n = 2$ $\qquad C_2 = 0.5$ N $\qquad C_1 = 0.75$ N

Substitution of values

$$E_{cell} = \frac{0.0591}{2} \log \frac{0.5}{0.75}$$
$$= \frac{0.0591}{2} \log \frac{2}{3}$$

$$= \frac{0.0591}{2} \times (-0.1760)$$

$$= \mathbf{-0.0052}$$

SOLVED PROBLEM 2. The emf of the cell set up as under was found to be 0.1182 volt at 25 °C. Calculate the solubility of AgCl.

$$Ag \mid \textit{Saturated Solution of AgCl} \parallel AgNO_3\,(0.001\ N) \mid Ag$$

SOLUTION :

Formula used

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Quantities given

$E_{cell} = 0.1182\,\text{V}$ $C_2 = 0.001$ $n = 1$

Substitution of values

$$0.1182 = \frac{0.0591}{n} \log \frac{0.001}{C_1}$$

or $$\log \frac{0.001}{C_1} = \frac{0.1182}{0.0591} = 2$$

or $$\frac{0.001}{C_1} = \text{antilog } 2 = 100$$

or $$C_1 = \frac{0.001}{100} = 1 \times 10^{-5} \text{ g mol}^{-1}$$

∴ $$\text{Solubility, } C_1 = 1 \times 10^{-5} \times 143.5 \text{ g lit}^{-1} = \mathbf{1.435 \times 10^{-3} \text{ g lit}^{-1}}$$

SOLVED PROBLEM 3. The emf of the following cell,

$$Hg \mid Hg_2Cl_2, KCl\ (Sat) \parallel H^+\ (a_1)\ \text{Quinhydrone} \mid Pt$$

was found to be 0.228 volt at 25 °C. Calculate the pH *of the solution.* (E_{cal} = *0.2415 Volt*)

SOLUTION :

Formula used

$$\text{pH} = \frac{0.4581 - E_{cell}}{0.0591}$$

Quantities given

$$E_{cell} = 0.228\ \text{V}$$

Substitution of values

$$pH = \frac{0.4581 - 0.228}{0.0591} = \mathbf{3.89}$$

SOLVED PROBLEM 4. The emf of the cell set up by using an acid solution, standard calomel electrode and quinhydrone electrode, was found to be 0.1595 volt at 25 °C. Calculate the *pH* of the acid solution. (emf of standard calomel electrode = – 0.2440 V and emf quinhydrone electrode = – 0.6990 V)

SOLUTION :

Formula used

$$E_{cell} = \left[E_{\mathbf{Q+}} - \frac{2.303\,RT}{n}\,pH\right] - E_{SCE}$$

Quantities given

$E_{\mathbf{Q+}} = 0.6990$ V

$E_{SCE} = -0.2440$

$\dfrac{2303\,RT}{F} = 0.0591$

$E_{cell} = 0.1595$

Substitution of values

$$\begin{aligned} 0.1595 &= [\,0.6990 - 0.0591\,pH\,] - 0.2440 \\ 0.1595 &= 0.6990 - 0.0591\,pH - 0.2440 \\ 0.1595 &= 0.4550 - 0.0591\,pH \end{aligned}$$

or
$$\begin{aligned} pH &= \frac{0.4550 - 0.1595}{0.0591} \\ &= \mathbf{5} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the single electrode potential for copper metal in contact with 0.1 M Cu^{2+} solution. $E^{o}_{Cu^{2+}/Cu}$ is 0.34 volt.

SOLUTION :

Formula used

$$E = E^{o} - \frac{0.0591}{n}\log[Cu^{2+}]$$

Quantities given

$E^{o}_{Cu^{2+}/Cu} = 0.34$ V $[Cu^{2+}] = 0.1$ M $n = 2$

Substitution of values

$$\begin{aligned} E &= 0.34\text{ V} - \frac{0.0591}{2}\log 0.1 \\ &= 0.34\text{ V} - 0.02955 \times (-1) \\ &= \mathbf{0.36955\ V} \end{aligned}$$

SOLVED PROBLEM 6. Hydrogen electrode and normal calomel electrode when immersed in a solution at 25 °C showed a potential of 0.664 V. Calculate the *pH* of the solution.

SOLUTION :

Formula used

$$E_{cell} = 0.2415 + 0.0591 \times pH$$

Quantities given

$$E_{cell} = 0.664\text{ V}$$

Substitution of values

$$0.664\text{ V} = 0.2415 + 0.0591\,pH = \frac{0.664 - 0.2415}{0.0591} = \mathbf{7.1489}$$

SOLVED PROBLEM 7. What will be the reaction in the cell which is made by combining standard Cd half cell with standard Cu half cell ? Also calculate the emf of the cell. The standard oxidation potential of half cells are 0.453 and – 0.337 V.

SOLUTION : The cell reactions are

$$\begin{aligned} & Cu \longrightarrow Cu^{2+} + 2e^- \\ & Cd^{2+} + 2e^- \longrightarrow Cd \\ \text{Net Reaction :}\quad & Cd^{2+} + Cu \longrightarrow Cu^{2+} + Cd \end{aligned}$$

Formula used

$$E_{cell} = \textit{Reduction potential of cathode} - \textit{Reduction potential of anode}$$

Quantities given

Reduction potential of cathode = – 0.337 V

Reduction potential of anode = 0.453 V

Substitution of values

$$\begin{aligned} E_{cell} &= -0.337\ V - 0.453\ V \\ &= \mathbf{-0.790\ V} \end{aligned}$$

SOLVED PROBLEM 8. Calculate the emf of the cell :

$$Ag_{(s)}\ |\ Ag^{+}(a = 0.1)\ ||\ Zn^{2+}(a = 0.1)\ |\ Zn_{(s)}$$

Given $E^o_{Ag/Ag+} = 0.799$ V $\qquad E^o_{Zn^{2+}/Zn} = 0.763$ V

Is the reaction spontaneous ?

SOLUTION :

Formula used

$$\textit{EMF of the cell} = E_R - E_L$$

Quantities given

$E_R = -0.763$ V $\qquad E_L = 0.799$ V

Substitution of values

$$\begin{aligned} \textit{EMF of the cell} &= -0.763\ V - (0.799\ V) \\ &= \mathbf{-1.562\ V} \end{aligned}$$

Since the emf of the cell is negative, the reaction is not spontaneous.

SOLVED PROBLEM 9. Calculate the free energy change of the following cell at 25 ºC.

$$Sn\ |\ Sn^{2+}(0.5N)\ ||\ Pb^{2+}(0.3N)\ |\ Pb$$

The standard emf of the cell is 0.14 V.

SOLUTION :

Formula used

$$\Delta G = -n F E$$

Quantities given

$n = 2 \qquad F = 96500 \qquad E = 0.14$ V

Substitution of values

$$\begin{aligned} \Delta G &= 2 \times 96500 \times 0.14\ J \\ &= \mathbf{27020\ J} \end{aligned}$$

SOLVED PROBLEM 10. When hydrogen electrode and normal calomel electrode are immersed in a solution at 25 °C, a potential of 0.624 is obtained. Calculate the *pH* of the solution.

SOLUTION :

Formula used

$$pH = \frac{E_{cell} - 0.2415}{0.0591}$$

Quantities given

$$E_{cell} = 0.624 \text{ V}$$

Substitution of values

$$\text{pH} = \frac{0.624 - 0.2415}{0.0591}$$

$$= \mathbf{6.47}$$

SOLVED PROBLEM 11. The standard reduction potential of Cu^{2+}/Cu and Ag^{+}/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^{+} will the emf of solution at 25 °C be zero if the concentration of Cu^{2+} is 0.01 M ?

SOLUTION : (i) To calculate the emf of the cell

The cell would be

$$\text{Cu} \mid Cu^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid \text{Ag}$$

and the cell reactions are

$$\text{LHE:} \quad \text{Cu} \longrightarrow Cu^{2+}_{(aq)} + 2e^{-} \qquad E^{o} = 0.337 \text{ V}$$

$$\text{RHE:} \quad Ag^{+}_{(aq)} + e^{-} \longrightarrow \text{Ag} \qquad E^{o} = 0.799 \text{ V}$$

The net cell reaction is

$$\text{Cu} + 2Ag^{+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2\text{Ag}$$

EMF of the cell is

$$EMF = E^{o}_{Right} - E^{o}_{Left}$$

$$= 0.799 \text{ V} - 0.337 \text{ V}$$

$$= \mathbf{0.462 \text{ V}}$$

(ii) To calculate the concentration of Cu^{2+} ions

Formula used

$$E_{cell} = E^{o}_{Cell} - \frac{0.0591}{n} \log \frac{[Cu^{2+}]}{[Ag^{+}]^{2}}$$

Quantities given

$E_{cell} = 0$ $\quad n = 2$ $\quad [Cu^{2+}] = 0.01 \text{ M}$ $\quad E^{o}_{cell} = 0.462 \text{ V}$

Substitution of values

$$0 = 0.462 \text{ V} - \frac{0.0591}{2} \log \frac{0.01}{[Ag^{+}]^{2}}$$

or

$$\log \frac{0.01}{[Ag^{+}]^{2}} = \frac{2 \times 0.462}{0.0591}$$

$$= 14.9577$$

or $$\frac{0.01}{[Ag^+]^2} = \text{Antilog } 14.9577$$

$$= 9.072 \times 10^{14}$$

or $$[Ag^+] = \sqrt{\frac{0.01}{9.072 \times 10^{14}}}$$

$$= \sqrt{1.099 \times 10^{-17}}$$

$$= \sqrt{10.099 \times 10^{-18}}$$

$$= \mathbf{3.178 \times 10^{-9}\ M}$$

SOLVED PROBLEM 12. Zinc granules are added in excess to 500 ml of 1.0 M nickel nitrate solution at 25 °C until the equilibrium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni are – 0.75 V are – 0.24 V respectively, find out the concentrations of Ni^{2+} ions in the solution at equilibrium.

SOLUTION : (i) To calculate the emf of the cell

Formula used

$$E_{cell} = E_{right} - E_{Left}$$

$$= (-0.24\text{ V}) - (-0.75\text{ V})$$

$$= 0.51\text{ V}$$

(ii) To calculate the concentration of Ni^{2+} ions

Formula used

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Ni^{2+}]}$$

Quantities given

E_{cell} *(at equilibrium)* $= 0$ $E^o_{cell} = 0.51$ V $n = 2$

Substitution of values

$$0 = 0.51 - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Ni^{2+}]}$$

or $$\log \frac{[Zn^{2+}]}{[Ni^{2+}]} = \frac{2 \times 0.51}{0.0591}$$

$$= 17.2589$$

or $$\frac{[Zn^{2+}]}{[Ni^{2+}]} = \text{Antilog } 17.2589$$

$$= 1.815 \times 10^{17}$$

Let x be the concentration Ni^{2+} at equilibrium, we have

$$Zn_{(s)} + Ni^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Ni_{(s)}$$

At Equilibrium x $1 - x$

or $$\frac{1 - x}{x} = 1.815 \times 10^{17}$$

or $$x = \mathbf{5.51 \times 10^{-18}}$$

SOLVED PROBLEM 13. For the galvanic cell

$$\text{Ag} \mid \text{AgCl}_{(s)}\,\text{KCl}\,(0.2\text{ M}) \parallel \text{K Br}\,(0.001\text{ M})\,\text{AgBr}_{(s)} \mid \text{Ag}$$

Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25 °C. K_{sp} AgCl $= 2.8 \times 10^{-10}$, K_{sp} AgBr $= 3.3 \times 10^{-13}$.

SOLUTION : The cell reactions are

Anode : $\text{Ag} + \text{Cl}^- \longrightarrow \text{AgCl} + e^-$

Cathode : $\text{AgBr} + e^- \longrightarrow \text{Ag} + \text{Br}^-$

Net Reaction : $\text{AgBr} + \text{Cl}^- \longrightarrow \text{AgCl} + \text{Br}^-$

Formula used

$$E_{cell} = E_{right} - E_{left}$$

$$= \left[E^o - \frac{2.303}{n\,F} \log\,[Ag^+]\right] - \left[E^o - \frac{2.303}{n\,F} \log\,[Ag^+]\right]$$

Quantities given

$[Ag^+]$ in left hand electrode $= \dfrac{K_{sp}\,(\text{AgCl})}{[\text{Cl}^-]} = \dfrac{2.8 \times 10^{-10}}{0.2} = 1.4 \times 10^{-9}\text{ mol lit}^{-1}$

$[Ag^+]$ in right hand electrode $= \dfrac{K_{sp}\,(\text{AgBr})}{[\text{Br}]} = \dfrac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10}\text{ mol lit}^{-1}$

$n = 1$

Substitution of values

$$E_{cell} = \left[E^o - \frac{2.303}{nF} \log\, 3.3 \times 10^{-10}\right] - \left[E^o - \frac{2.303}{nF} \log\, 1.4 \times 10^{-9}\right]$$

$$= \frac{0.0591}{1} \log \frac{1.4 \times 10^{-9}}{3.3 \times 10^{-10}}$$

$$= \mathbf{-\,0.037\ V}$$

Since E_{cell} is –ve, the cell reaction is non-spontaneous. The reverse reaction will be spontaneous.

SOLVED PROBLEM 14. The standard reduction potential for the half cell

$$\text{NO}_{3\,(aq)}^{-} + 2\text{H}^+_{(aq)} + e^- \longrightarrow \text{NO}_{2\,(g)} + \text{H}_2\text{O}$$

is 0.78 V.

(i) Calculate the reduction potential in 8 M H$^+$.

(ii) What will be the reduction potential of the half cell in neutral solution? Assume all other species to be at unit concentration.

SOLUTION : (i) To calculate the reduction potential in 8 M H$^+$.

Formula used

$$E = E^o - \frac{0.059}{n} \log K$$

where

$$K = \frac{[NO_2]\,[H_2O]}{[NO_3^-]\,[H^+]}$$

Quantities gives

$E^o = 0.78$ V $\qquad n = 1 \qquad [H^+] = 8$ M

Substitution of values

$$E = 0.78 - \frac{0.0591}{1} \log \frac{1}{(8)^2}$$
$$= 0.78 - 0.0591 \times (-1.806)$$
$$= 0.78 + 0.1067$$
$$= \mathbf{0.8867\ V}$$

(ii) To calculate the reduction potential of the half cell in neutral Solution

Formula used

$$E = E^o - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

Quantities given

$E^o = 0.78$ V $\quad n = 1 \quad [H^+] = 10^{-7}$

Substitution of values

$$E = 0.78 - \frac{0.0591}{1} \log \frac{1}{(10^{-7})^2}$$
$$= 0.78 - 0.0591 \times 14$$
$$= 0.78 - 0.8274$$
$$= \mathbf{-0.0474}$$

SOLVED PROBLEM 15. The Edison storage cell is represented as

$$Fe_{(s)} \mid FeO_{(s)} \mid KOH_{(aq)} \parallel Ni_2O_{3\,(s)} \mid Ni_{(s)}$$

The half cell reactions are

$$Ni_2O_{3\,(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2NiO_{(s)} + 2OH^- \qquad E^o = 0.40\ V$$
$$FeO_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow Fe_{(s)} + 2OH^- \qquad E^o = -0.87\ V$$

(i) What is the cell emf ?

(ii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?

SOLUTION : (i) To calculate the cell emf

Formula used

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Products]}{[Reactants]}$$

Quantities given

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.40 - (-0.87) = 1.27$ V $\quad n = 1$

$[Products] = 1 \quad [Reactants] = 1$

Substitution of values

$$E_{cell} = 1.27\ V - \frac{0.0591}{1} \log 1$$
$$= \mathbf{1.27\ V}$$

(ii) To calculate the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?

Formula used

$$W_{elect} = n F E$$

Quantities gives

$n = 2$ $\quad F = 96500$ $\quad E = 1.27$ V

Substitution of values

$$W_{elect} = 2 \times 96500 \times 1.27$$
$$= \mathbf{2.451 \times 10^5\ J}$$

SOLVED PROBLEM 16. Calculate EMF of the following cell at 20 °C ;

$$\text{Zn} \mid \text{Zn}^{2+}\ (a = 0.0004) \parallel \text{Cd}^{2+}\ (a = 0.2) \mid \text{Cd}$$

E^o for Zinc and Cadmium electrodes are – 0.76 and – 0.40 volts respectively.

SOLUTION : The cell reactions are

At Anode : $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$

At Cathode : $\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$

Net Reaction : $\text{Zn} + \text{Cd}^{2+} \longrightarrow \text{Cd} + \text{Zn}^{2+}$

(i) To calculate E° of the cell

Formula used

$$E^o_{cel} = E^o_{right} - E^o_{left}$$

Quantities given

$E^o_{right} = -0.40$ $\quad E^o_{left} = -0.76$

Substitution of values

$$E^o_{cel} = -0.40 - (-0.76\text{ V})$$
$$= 0.36\text{ V}$$

(ii) To calculate EMF of the cell

Formula used

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cd^{2+}]}$$

Quantities given

$E^o_{cell} = 0.36$ V $\quad n = 2$ $\quad [Zn^{2+}] = 0.0004$ $\quad [Cd^{2+}] = 0.2$

Substitution of values

$$E_{cell} = 0.36 - \frac{0.0591}{2} \log \frac{0.0004}{0.2}$$
$$= 0.36 - 0.02955 \log 0.0002$$
$$= 0.36 - 0.02955 \times (-2.6989)$$
$$= 0.36 + 0.07975$$
$$= \mathbf{0.4397\ V}$$

SOLVED PROBLEM 17. An excess of liquid mercury is added to an acidified solution of 1.0 × 10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25 °C. Calculate $E^o_{Hg^{2+}/Hg}$, assuming that the only reaction that occurs is

$$2\text{Hg} + 2\text{Fe}^{3+} \longrightarrow \text{Hg}_2^{2+} + 2\text{Fe}^{2+}$$

Given $E^o_{Fe^{3+}/Fe^{2+}} = 0.77$ V

SOLUTION : The cell reaction is

	$2\,Hg \; + \; 2Fe^{3+}$	$\longrightarrow$	$Hg_2^{\;2+}$	$+ \; 2Fe^{2+}$
Initial conc.	1.0×10^{-3} M			
Equilibrium conc.	0.05×10^{-3} M		$\dfrac{0.95 \times 10^{-3}}{2}$	0.95×10^{-3} M

Formula used

$$E = \left[E^o_{Fe^{3+}/Fe^{2+}} - E^o_{Hg_2^{2+}/Hg}\right] - \frac{0.0591}{n} \log \frac{[Hg_2^{\;2+}]\;[Fe^{2+}]^2}{[Fe^{3+}]^2}$$

Quantities given

$E^o_{Fe^{3+}/Fe^{2+}} = 0.77$ V

$n = 2$

$[Hg_2^{\;2+}] = \dfrac{0.95 \times 10^{-3}}{2}$

$[Fe^{2+}] = 0.95 \times 10^{-3}$

$[Fe^{3+}] = 0.05 \times 10^{-3}$

$E = 0$

Substitution of values

$$E = \left[0.77 - E^o_{Hg_2^{2+}/Hg}\right] - \frac{0.0591}{2} \log \frac{\dfrac{0.95 \times 10^{-3}}{2} \times (0.95 \times 10^{-3})^2}{(0.05 \times 10^{-3})^2}$$

$$E^o_{Hg_2^{2+}/Hg} = 0.77 - 0.02955 \log 0.00857$$

$$= \mathbf{0.831\ V}$$

ADDITIONAL PRACTICE PROBLEMS

1. Calculate the maximum possible electric work that can be obtained from the following cell under standard conditions at 25 °C

$$Zn \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu$$

Given $E^o_{Zn^{2+}_{(aq)}/Zn} = -0.76$ V $\quad E^o_{Cu^{2+}/Cu} = 0.34$ V

Answer. – 212.3 kJ mol^{-1}

2. A Galvanic cell consists of metallic zinc plate immersed in 0.1 M zinc nitrate solution and lead plate in 0.02 M lead nitrate solution. Calculate the emf of the cell at 25 °C. Write the chemical equations of the electrode reactions. $E^o_{Zn^{2+}/Zn} = -0.76$ V , $E^o_{Pb^{2+}/Pb} = -0.13$ V

Answer. 0.6095 V

3. For a cell

$$Ag_{(s)} \mid AgNO_3\ (0.01\ M) \parallel AgNO_3\ (1.0\ M) \mid Ag_{(s)}$$

(a) Calculate the emf at 25 °C

(b) Will the cell generate emf when two concentrations become equal.

Answer. 0.1184 V , No

4. Calculate the standard electrode potential of Ni^{2+}/Ni electrode, if the cell potential of the cell

$$Ni \mid Ni^{2+}\ (0.01\ M) \parallel Cu^{2+}\ (0.1\ M) \mid Cu$$

is 0.59 V.

Answer. – 0.2205 V

5. Calculate the emf of the cell

$$Cr \mid Cr^{3+}\ (0.1\ M) \parallel Fe^{2+}\ (0.01\ M) \mid Fe$$

Given $E^o_{Cr^{3+}/Cr} = 0.75$ V $\quad E^o_{Fe^{2+}/Fe} = -0.45$ V

Answer. 0.2607 V

6. Determine the equilibrium constant of the following reaction at 298 K

$$2Fe^{3+} + Sn \rightleftharpoons 2Fe^{2+} + Sn^{4+}$$

From the obtained value of equilibrium constant predict whether Sn^{2+} ion can reduce Fe^{3+} to Fe^{2+} quantitatively or not.

Answer. 1.4215×10^{31}

7. The following reaction takes place in the cell

$$Zn_{(s)} + Co^{2+} \rightleftharpoons Co_{(s)} + Zn^{2+}$$

Write down the electrode reactions and calculate the standard emf of the cell. Given that

$E^o_{Zn/Zn^{2+}} = 0.76$ V, $E^o_{Co/Co^{2+}} = 0.28$ V

Answer. 0.48 V

8. Consider the cell

$$Zn \,|\, Zn^{2+}_{(aq)}\ 0.1\ M \,||\, Cu^{2+}_{(aq)}\ 1M \,|\, Cu$$

The standard reduction potentials are 0.35 V for

$$Cu_{(aq)} + 2e^- \longrightarrow Cu$$

and – 0.763 V for

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn$$

(i) Write down the cell reactions

(ii) Calculate the emf of the cell

(iii) Is the cell reaction spontaneous or not ?

Answer. 1.113, spontantaneous

9. A cell contains two hydrogen electrodes. The negative electrode is in contact with solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 volt at 25 ºC. Calculate the concentration of H^+ ion at positive electrode ?

Answer. 1×10^{-4} M

10. The standard reduction potential of Ag^+/Ag electrode at 298 K is 0.799 V. Given that for Ag I, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of Ag I

Answer. 0.325 V

11. The standard reduction potential at 25 ºC of the reaction

$$2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2$$

is – 0.8277 V. Calculate the equilibrium constant for the reaction :

$$2H_2O \rightleftharpoons H_3^+O + OH^- \text{ at } 25\ ^oC$$

Answer. 1×10^{-14}

12. Calculate the emf of the following cells at 25 ºC

(a) $Mg_{(s)} \,|\, Mg^{2+}\ (0.001\ M) \,||\, Cu^{2+}\ (0.0001\ M) \,|\, Cu_{(s)}$

(b) $Fe_{(s)} \,|\, Fe^{3+}\ (0.00\ M) \,||\, H^+\ (1\ M) \,|\, H_2\ (1\ atm)\ Pt$

Given $E^o_{Mg^{2+}/Mg} = -2.37$ V, $E^o_{Cu^{2+}/Cu} = +0.34$ V, $E^o_{Fe^{3+}/Fe} = -0.44$ V

Answer. (a) 2.6805 V (b) – 0.5286 V

13. Calculate the emf of a cell containing two hydrogen electrodes, the negative one is in contact with 10^{-6} M OH^- ions and the positive one is in contact with 0.05 M H^+.

Answer. 0.395 V

30

Photochemistry

CHAPTER

KEY CONCEPTS AND EQUATIONS

PHOTOCHEMICAL REACTION

A reaction which takes place by absorption of visible and ultraviolet radiations is called a photochemical reaction and the branch of chemistry which deals with the study of photochemical reactions is called Photochemistry.

LIGHT ABSORPTION

When light is passed though a medium, a part of it is absorbed. The photochemical reactions are caused by the absorbed light. The intensity of radiation can be defined as the number of photons that pass across a unit area in unit time. Mathematically,

$$\frac{dN}{N} = b\,dx = -\frac{dI}{I}$$

where N is the number of incident photons, dN, is the number of photons absorbed in thickness dx, I is the intensity of incident light, $-\,dI$ is the reduction in the intensity of incident light, and b is proportionately constant called absorption constant.

When $x = 0$, $I = I_0$. On integration we get

$$I = I_0(-b\,x)$$

or

$$\text{In}\left(\frac{I}{I_0}\right) = -b\,x$$

This relationship is called **Lambert Law.**

This equation was extended to solution of compounds in transparent solvent and takes the form

$$\text{In}\left(\frac{I}{I_0}\right) = \in Cx$$

where c is the molar concentration, $\in$ is a constant characteristic of the solute called the absorption coefficient. This new relationship is called **Lambert-Beer Law.**

LAWS OF PHOTOCHEMISTRY

Grothus-Draper Law

According to this law it is only the absorbed light radiations that are effective in producing a chemical reaction. This law is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and molecules undergoing change.

Stark Einstein Law

According to this law each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the product in a photochemical reaction.

QUANTUM YIELD OR QUANTUM EFFICIENCY

The number of molecules reacted or formed per photon of light absorbed is called Quantum yield. It is denoted by ϕ so that

$$\phi = \frac{\text{No. of molecules reacted or formed}}{\text{No. of photons absorbed.}}$$

THE ENERGY OF PHOTONS : EINSTEIN

The energy of a photon (or quantum), E, is given by the equation

$$E = hv = \frac{h\,v}{\lambda}$$

where h is Planck's constant (6.625×10^{-27}), v is the frequency of radiation, λ is the wavelength of radiation and c is the velocity of light (3.0×10^{10} cm sec^{-1}) The energy, E, of an Avogadro's Number (N) of photons is referred to as one einstein. That is

$$E = \frac{N\,h\,c}{\lambda}$$

Substituting $N = 6.02 \times 10^{23}$, $h = 6.625 \times 10^{-27}$ and $c = 3.0 \times 10^{10}$ cm sec^{-1}, we have

$$E = \frac{1.196 \times 10^{8}}{\lambda} \text{ erg mol}^{-1}$$

If λ is expressed in Å unit ($1\text{Å} = 10^{-8}$ cm), we get

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1}$$

since $1 \text{ cal} = 4.184 \times 10^{7}$ erg, energy in calories would be

$$E = \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^{7}} \text{ cal mol}^{-1}$$

$$= \frac{2.859 \times 10^{5}}{\lambda} \text{ cal mol}^{-1}$$

It is clear that numerical value of einstein varies inversely with the wavelength[10] of radiations.

ADDITIONAL PRACTICE PROBLEMS

SOLVED PROBLEM 1. Calculate the energy of one einstein of a light of wavelength 3000 Å.

SOLUTION :

Formula used

$$E = \frac{2.859 \times 10^{5}}{\lambda} \text{ kcal mol}^{-1}$$

Quantity given

$$\lambda = 3000 \text{ Å}$$

Substitution of value

$$E = \frac{2.859 \times 10^{5}}{3000}$$

$$E = \mathbf{95.3 \text{ kcal mol}^{-1}}$$

SOLVED PROBLEM 2. Calculate the energy of a photon corresponding to wavelength 3600 Å. ($h = 6.63 \times 10^{-27}$ erg sec ; $c = 3 \times 10^{10}$ cm sec^{-1})

SOLUTION :

Formula used

$$E = \frac{hc}{\lambda}$$

Quantities given

$h = 6.63 \times 10^{-27}$ erg sec $\quad c = 3 \times 10^{10}$ cm sec^{-1} $\quad \lambda = 3600$ Å $= 3600 \times 10^{-8}$ cm

Substitution of values

$$E = \frac{6.63 \times 10^{-27} \times 3 \times 10^{10}}{3600 \times 10^{-8}} \text{ erg}$$

$$= \frac{19.89 \times 10^{-17}}{10^{-8} \times 3600 \times 4.184 \times 10^{7}} \text{ cal} \qquad [\because 1 \text{ cal} = 4.184 \times 10^{7} \text{ erg}]$$

$$= \mathbf{1.320 \times 10^{-19} \text{ cal}}$$

SOLVED PROBLEM 3. A radiation of 2530 Å incident on HI results in the decomposition of 1.85 × 10^{-2} mole per 1000 cal of radiant energy. Calculate the quantum efficiency.
($N = 6.023 \times 10^{23}$; $h = 6.62 \times 10^{-27}$; $c = 3 \times 10^{10}$ cm sec^{-1})

SOLUTION : (i) To calculate the number of einsteins absorbed

Formula used

$$\textit{No. of einsteins absorbed} = \frac{\textit{Total Energy absorbed}}{\dfrac{N\,h\,c}{\lambda}}$$

Quantities given

Total energy absorbed $= 1000\ cal = 1000 \times 4.184 \times 10^{7}\ erg$ $\qquad$ N $= 6.023 \times 10^{23}$

$h = 6.62 \times 10^{-27}$ $\qquad c = 6.62 \times 10^{-27}$ $\qquad \lambda = 2530$ Å $= 2530 \times 10^{-8}$ cm

Substitution of values

$$\text{No. of einstein absorbed} = \frac{1000 \times 4.184 \times 10^{7} \times 2530 \times 10^{-8}}{6.023 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}$$

$$= 8.849 \times 10^{-3}$$

(ii) To calculate the quantum efficiency

Formula used

$$\phi = \frac{\textit{No. of moles of HI decomposed}}{\textit{No. of einsteins absorbed}}$$

Quantities given

No. of moles of HI decomposed $= 1.85 \times 10^{-2}$ mole

No. of einsteins absorbed $= 8.849 \times 10^{-3}$

Substitution of values

$$\phi = \frac{1.85 \times 10^{-2}}{8.849 \times 10^{-3}}$$

$$= \mathbf{2.09}$$

SOLVED PROBLEM 4. Calculate the value of one einstein for light having $\lambda = 2000$ Å.

SOLUTION :

Formula used

$$E = \frac{2.859 \times 10^{5}}{\lambda}$$

Quantity given $\lambda = 2000$ Å

Substitution of values

$$E = \frac{2.859 \times 10^5}{2000}$$

$$= \mathbf{142.95\ kcal}$$

SOLVED PROBLEM 5. If the value of an einstein is 1.594×10^4 k J, find the value of wavelength of radiation.

SOLUTION :

Formula used

$$\textit{Energy per einstein} = \frac{N\,h\,c}{\lambda}$$

Quantities given

$\textit{Energy per einstein} = 1.594 \times 10^4$ kJ $\qquad c = 3 \times 10^{10}$ cm sec^{-1}

$= 1.594 \times 10^{14}$ erg

$h = 6.62 \times 10^{-27}$ erg sec $\qquad N = 6.02 \times 10^{23}$

Substitution of values

$$1.594 \times 10^{14}\ \text{kJ} = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27}\ \text{erg sec} \times 3 \times 10\ \text{cm sec}^{-1}}{\lambda}$$

$$\lambda = \frac{119.55 \times 10^6}{1.594 \times 10^{14}}$$

$$= 75 \times 10^{-8}\ \text{cm}$$

$$= \mathbf{75\ Å}$$

SOLVED PROBLEM 6. Calculate the energy of the photon corresponding to wavelength 4800 Å. ($h = 6.624 \times 10^{-27}$ erg sec ; $c = 3 \times 10^{10}$ cm sec^{-1})

SOLUTION :

Formula used

$$E = \frac{h\,c}{\lambda}$$

Quantities given

$h = 6.624 \times 10^{-27}$ erg sec $\qquad c = 3 \times 10^{10}$ cm sec^{-1} $\qquad \lambda = 4800$ Å $= 4800 \times 10^{-8}$ cm

Substitution of values

$$E = \frac{6.624 \times 10^{-27} \times 3 \times 10^{10}}{4800 \times 10^{-8}}\ \text{erg}$$

$$= 4.14 \times 10^{-12}\ \text{erg}$$

$$= \frac{4.14 \times 10^{-12}}{4.184 \times 10^7}\ \text{cal} \qquad [\ \because 1\ \text{cal} = 4.184 \times 10^7\ \text{erg}]$$

$$= 0.9895 \times 10^{-19}\ \text{cal}$$

$$= \mathbf{0.9895 \times 10^{-22}\ kcal}$$

SOLVED PROBLEM 7. In the photochemical reaction $\text{B} \longrightarrow \text{C}$, 1.00×10^{-5} mole of C is formed as a result of the absorption of 6.00×10^7 ergs at 3600 Å. Calculate the quantum yield.

SOLUTION :

Formula used

$$\textit{Quantum efficiency} = \frac{\textit{No. of moles of C formed}}{\textit{No. of einsteins absorbed}}$$

Quantities given

$$\textit{No. of moles of C formed} = 1.00 \times 10^{-5}\text{ mole}$$

$$\begin{aligned}\textit{No. of einsteins absorbed} &= \frac{\textit{Energy absorbed}}{\textit{Energy per einstein}}\\ &= \frac{6.0 \times 10^{7}\text{ erg}}{\dfrac{1.196\times10^{16}}{\lambda}\text{ erg}}\\ &= \frac{6.0 \times 10^{7} \times 3600}{1.196 \times 10^{16}} \qquad [\because \lambda = 3600\text{ Å}]\\ &= 1.806 \times 10^{-5}\end{aligned}$$

Substitution of values

$$\begin{aligned}\text{Quantum efficiency, } \phi &= \frac{1.00 \times 10^{-5}}{1.806\times 10^{-5}}\\ &= \mathbf{0.553}\end{aligned}$$

SOLVED PROBLEM 8. For a photochemical reaction A ⟶ B, 1.0×10^{-5} mole of B were formed on absorption of 6.0×10^{7} ergs at 3600 Å. Calculate the quantum efficiency of the reaction. ($N = 6.62 \times 10^{23}$; $h = 6.62 \times 10^{-27}$ erg sec)

SOLUTION :

Formula used

$$\textit{Quantum efficiency} = \frac{\textit{No. of moles of B formed}}{\textit{No. of einsteins absorbed}}$$

Quantities given

$$\textit{No. of moles of B formed} = 1.00 \times 10^{-5}\text{ mole}$$

$$\begin{aligned}\textit{No. of einsteins absorbed} &= \frac{\text{Energy absorbed}}{\text{Energy per einstein}}\\ &= \frac{6.0 \times 10^{7}\text{ erg}}{\dfrac{1.196 \times 10^{16}\text{ erg}}{\lambda}} \qquad \left[\because 1\text{ einstein} = \frac{1.196 \times 10^{16}\text{ erg}}{\lambda}\right]\\ &= \frac{6.0 \times 10^{7} \times 3600}{1.196 \times 10^{16}} \qquad [\because \lambda = 3600\text{ Å}]\\ &= 1.806 \times 10^{-5}\end{aligned}$$

Substitution of values

$$\begin{aligned}\text{Quantum efficiency, } \phi &= \frac{1.0 \times 10^{-5}}{1.806 \times 10^{-5}}\\ &= \mathbf{0.553}\end{aligned}$$

SOLVED PROBLEM 9. A certain system absorbs 2×10^{16} quanta of light per second. On irradiation for 10 minutes 0.001mole of the reactant was found to have reacted. Calculate quantum yield for the process. (Avogadro's No. $= 6.024 \times 10^{23}$)

SOLUTION :

Formula used

$$\phi = \frac{\textit{No. of molecules decomposed}}{\textit{No. of photons absorbed}}$$

Quantities given

$$\text{No. of molecules decomposed} = 0.001 \times 6.024 \times 10^{23} \text{ molecules}$$

$$\begin{aligned}\text{No. of photons absorbed in 10 minutes} &= \text{No. of photons absorbed per second} \times \text{No. of seconds}\\ &= 2 \times 10^{16} \times 600\end{aligned}$$

Substitution of values

$$\begin{aligned}\phi &= \frac{0.001 \times 6.024 \times 10^{23}}{2 \times 10^{16} \times 600}\\ &= \mathbf{50.2}\end{aligned}$$

SOLVED PROBLEM 10. Calculate the values of frequency, quantum energy and einstein for 500 nm radiation.

SOLUTION : (i) To calculate the value of frequency

Formula used

$$\upsilon = \frac{c}{\lambda}$$

Quantities given

$c = 3 \times 10^{10} \text{ cm sec}^{-1}$ $\lambda = 500 \text{ nm} = 500 \times 10^{-9} \text{m} = 500 \times 10^{-7} \text{ cm}$

Substitution of values

$$\begin{aligned}\upsilon &= \frac{3 \times 10^{10}}{500 \times 10^{-7}}\\ &= \mathbf{6 \times 10^{14}}\end{aligned}$$

(ii) To calculate the quantum energy

Formula used

$$E = \frac{h\,c}{\lambda}$$

Quantities given

$h = 6.62 \times 10^{-27} \text{ erg sec}$ $c = 3 \times 10^{10} \text{ cm sec}^{-1}$ $\lambda = 500 \times 10^{-7} \text{ cm}$

Substitution of values

$$\begin{aligned}E &= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{500 \times 10^{-7}}\\ &= \mathbf{39.72 \times 10^{-13} \text{ erg}}\end{aligned}$$

(iii) To calculate the value of one einstein

Formula used

$$\textit{Energy per einstein} = \textit{Avogadro's No.} \times \textit{Energy per photon}$$

Quantities given

$\textit{Avogadro's No.} = 6.02 \times 10^{23}$ $\textit{Energy per photon} = 39.72 \times 10^{-11} \text{ erg}$

Substitution of values

$$\begin{aligned}\textit{Energy per einstein} &= 6.02 \times 10^{23} \times 39.72 \times 10^{-11} \text{ erg}\\ &= 2.39 \times 10^{14} \text{ erg mol}^{-1}\\ &= \frac{2.39 \times 10^{14}}{4.184 \times 10^{7}} \text{ cal mol}^{-1} \qquad [\because 1 \text{ cal} = 4.184 \times 10^{7} \text{ erg}]\\ &= 5.71 \times 10^{6} \text{ cal mol}^{-1}\\ &= \mathbf{5.71 \times 10^{3} \text{ kcal mol}^{-1}}\end{aligned}$$

SOLVED PROBLEM 11. In a photochemical combination of H_2 and Cl_2 a quantum yield of 1×10^6 is obtained with a wavelength of 4800 Å. How many moles of HCl would be produced under these conditions per calorie of radiation energy absorbed ?

SOLUTION : (i) To calculate no. of einsteins absorbed per cal of energy

Formula used

$$\textit{No. of einsteins} = \frac{\textit{Energy absorbed}}{\textit{Energy per einstein}}$$

Quantities given

$$\textit{Energy absorbed} = 1 \text{ cal} = 4.184 \times 10^{7} \text{ erg}$$

$$\textit{Energy per einstein} = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1}$$

$$\lambda = 4800 \text{ Å}$$

Substitution of values

$$\text{No. of einsteins} = \frac{4.184 \times 10^{7} \text{ erg} \times 4800}{1.196 \times 10^{16} \text{ erg mol}^{-1}}$$

$$= 1.679 \times 10^{-5}$$

(ii) To calculate the no. of moles of HCl produced

Formula used

$$\phi = \frac{\textit{No. of moles of HCl produced}}{\textit{No. of einsteins absorbed}}$$

Quantities given

$\phi = 1 \times 10^{6}$ $\qquad$ *No. of einsteins absorbed* $= 1.679 \times 10^{-5}$

Substitution of values

$$1 \times 10^{6} = \frac{\text{No. of moles of HCl produced}}{1.679 \times 10^{-5}}$$

or $\quad$ No. of moles of HCl produced $=$ **16.79 moles**

SOLVED PROBLEM 12. Calculate the energy in electron volt (eV) units of quantum of radiation of wavelength 1000 Å.

Velocity of light $= 3.0 \times 10^{10}$ cm sec^{-1}

$h = 6.62 \times 10^{-27}$ erg sec

$1 \text{ Å} = 10^{-8}$ cm

SOLUTION : $\qquad 1\, eV = 1.6 \times 10^{-12}$ erg

Solution :

Formula used

$$E = \frac{h\,c}{\lambda}$$

Quantities given

$h = 6.62 \times 10^{-27}$ erg sec $\qquad c = 3.0 \times 10^{10}$ cm sec^{-1} $\qquad \lambda = 1000 \text{ Å} = 1000 \times 10^{-8}$ cm

Substitution of values

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{1000 \times 10^{-8}} \text{ erg}$$

$$= 1.986 \times 10^{-11} \text{ erg}$$

$$= \frac{1.986 \times 10^{-11}}{1.6 \times 10^{-12}} \text{ eV} \qquad [\because 1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}]$$

$$= \mathbf{12.4125 \ eV}$$

SOLVED PROBLEM 13. A certain system absorbs 3×10^8 quanta of light per second. On irradiation for 400 seconds, 0.001 mole of the reactant was found to have reacted. Calculate the quantum yield for the process (Avogadro's No. = 6.02×10^{23}).

SOLUTION :

Formula used

$$\phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of photons of radiation energy absorbed}}$$

Quantities given

No. of molecules reacted $= 0.001 \times 6.02 \times 10^{23}$

No. of photons of energy absorbed = *No. of photons absorbed per second* × *No. of seconds*

$= 3 \times 10^8 \times 400$

Substitution of values

$$\phi = \frac{0.001 \times 6.02 \times 10^{23}}{3 \times 10^8 \times 400}$$

$$= \mathbf{50.16 \times 10^8}$$

SOLVED PROBLEM 14. The quantum yield for reaction $2\,HI \longrightarrow H_2 + I_2$ is 2. Calculate the number of photons absorbed in an experiment in which 0.01 mole of HI are decomposed. ($N = 6.02 \times 10^{23}$)

SOLUTION :

Formula used

$$\phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of photons absorbed}}$$

Quantities given

$\phi = 2$

No. of molecules reacted $= 0.01 \times 6.02 \times 10^{23}$

Substitution of values

$$2 = \frac{0.01 \times 6.02 \times 10^{23}}{\textit{No. of photons absorbed}}$$

$$\textit{No. of photons absorbed} = \frac{0.01 \times 6.02 \times 10^{23}}{2}$$

$$= \mathbf{3.01 \times 10^{21}}$$

SOLVED PROBLEM 15. Derive value of radiation of wavelength 3000 Å in :

(i) Wave number (ii) Frequency (iii) Quantum energy (iv) Einstein energy

SOLUTION : (i) To calculate wave number

Fomula used

$$\bar{\upsilon} = \frac{1}{\lambda}$$

Quantity given

$\lambda = 3000$ Å $= 3000 \times 10^{-8}$ cm

Substitution of value

$$\bar{\upsilon} = \frac{1}{3000 \times 10^{-8}\,\text{cm}}$$

$$= \mathbf{3.33 \times 10^4\ cm^{-1}}$$

(ii) To calculate frequency

Formula used

$$\upsilon = \frac{c}{\lambda}$$

Quantities given

$c = 3 \times 10^{10}$ $\lambda = 3000\ \text{Å} = 3000 \times 10^{-8}\ \text{cm}$

Substitution of values

$$\upsilon = \frac{3 \times 10^{10}\ \text{cm sec}^{-1}}{3000 \times 10^{-8}\ \text{cm}}$$

$$= 1 \times 10^{15}\ \text{sec}^{-1}$$

(iii) To calculate quantum energy.

Formula used

$$E = \frac{h\,c}{\lambda}$$

Quantities given

$h = 6.62 \times 10^{-27}\ \text{erg sec}$ $c = 3 \times 10^{10}\ \text{cm sec}^{-1}$ $\lambda = 3000 \times 10^{-8}\ \text{cm}$

Substitution of values

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{3600 \times 10^{-8}}\ \text{erg}$$

$$= \mathbf{5.516 \times 10^{-12}\ erg}$$

(iv) To calculate Einstein energy

Formula used

$$\textit{Einstein energy} = \textit{Avogadro's No.} \times \textit{Quantum energy}$$

Quantities given

Avogadro's No. $= 6.02 \times 10^{23}$ *Quantum energy* $= 6.62 \times 10^{-12}\ \text{erg}$

Substitution of values

$$E = 6.02 \times 10^{23} \times 6.62 \times 10^{-12}\ \text{erg}$$

$$= 3.985 \times 10^{12}\ \text{erg}$$

$$= \frac{3.985 \times 10^{12}}{4.184 \times 10^{7}}\ \text{cal} \qquad [\because 1\ \text{cal} = 4.184 \times 10^{7}\ \text{erg}]$$

$$= \mathbf{9.524 \times 10^{4}\ kcal}$$

SOLVED PROBLEM 16. A substance in a cell of length *l* absorbs 20% of the incident light. What fraction of light will be absorbed in a cell of length 5*l*.

SOLUTION :

Formula used

$$\log \frac{I}{I_o} = \frac{-kx}{2.303}$$

Quantities given

$\frac{I}{I_o} = 100 - 20\% = 80\% = 0.8$ $x = l$ in first case $x = 5l$ in second case

Substitution of values

$$\log A = \frac{-k \times l}{2.303} \qquad \text{....(i) for first case}$$

$$\log A = \frac{-k \times 5l}{2.303} \qquad \text{...(ii) for second case}$$

Dividing (i) by (ii) we get

$$\frac{\log 0.8}{\log A} = \frac{-k \times l}{2.303} \times \frac{2.303}{-k \times 5l}$$

or

$$\log A = 5 \times \log 0.8$$

$$= 5 \times (-0.0969)$$

$$= -0.4845$$

or $$A = \text{Antilog}(-0.4845) = 0.3277 = 32.77\%$$

SOLVED PROBLEM 17. A certain system absorbs 8.81×10^{8} ergs of radiation of the wavelength 2540 Å in a certain time. It is observed that 1.12×10^{-4} moles of the irradiated substance has reacted in the same time. What is the quantum efficiency of the process ?

$$N = 6.023 \times 10^{23} \qquad h = 6.625 \times 10^{-27} \qquad c = 2.998 \times 10^{10} \text{ cm sec}^{-1}$$

SOLUTION : (i) To calculate the energy per einstein

Formula used

$$\textit{Energy per einstein} = \frac{N\,h\,c}{\lambda}$$

Quantity given

$$N = 6.02 \times 10^{23} \quad h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 2.998 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 2540 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\text{Energy per einstein} = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 2.998 \times 10^{10}}{2540 \times 10^{-8}}$$

$$= 4.70 \times 10^{12} \text{ erg}$$

(ii) To calculate the quantum efficiency

Formula used

$$\phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of einsteins absorbed}}$$

Quantities given

$$\textit{No. of molecules reacted} = 1.12 \times 10^{-4} \text{ mole}$$

$$\textit{No. of einsteins absorbed} = \frac{\textit{Energy absorbed}}{\textit{Energy per einstein}}$$

$$= \frac{8.81 \times 10^{8} \text{ erg}}{4.70 \times 10^{12} \text{ erg}}$$

$$= 1.874 \times 10^{-4}$$

Substitution of values

$$\phi = \frac{1.12 \times 10^{-4}}{1.874 \times 10^{-4}}$$

$$= \mathbf{0.5977}$$

SOLVED PROBLEM 18. Radiation of wavelength of 2500 Å was passed through a cell containing 10 ml of a solution which was 0.05 molar in oxalic acid and 0.01 molar in uranyl sulphate. After absorption of 80 joules of radiation energy the concentration of oxalic acid was reduced to 0.04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

SOLUTION : (i) To calculate the number of photons absorbed

Formula used

$$\textit{No. of photons absorbed} = \frac{\textit{Energy absorbed}}{\textit{Energy per photon}}$$

Quantities given

$$\textit{Energy absorbed} = 80 \text{ Joules}$$

$$\text{Energy per photon} = \frac{h\,c}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{2500 \times 10^{-8} \times 10^{7}}\ J$$

$$= 7.944 \times 10^{-19} \text{ J}$$

Substitution of values

$$\text{No. of photon absorbed} = \frac{80\text{ J}}{7.944 \times 10^{-19}\text{ J}} = 1.007 \times 10^{20}$$

(ii) To calculate the quantum efficiency

Formula used

$$\textit{Quantum efficiency} = \frac{\textit{No. of molecules decomposed}}{\textit{No. of photons absorbed}}$$

Quantities given

$$\textit{No. of photons absorbed} = 1.007 \times 10^{20}$$

$$\textit{No. of molecules decomposed} = \frac{0.01 \times 10 \times 6.02 \times 10^{23}}{1000} = 6.02 \times 10^{19}$$

Substitution of values

$$\text{Quantum efficiency} = \frac{6.02 \times 10^{19}}{1.007 \times 10^{20}} = \mathbf{0.598}$$

SOLVED PROBLEM 19. A certain system absorbs 3.0×10^{16} quantum of light per second on irradiation for 10 minutes. 0.002 mole of reactant was found to have reacted. Calculate the quantum efficiency of the process. ($N = 6.023 \times 10^{23}$)

SOLUTION :

Formula used

$$\phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of einsteins absorbed}}$$

Quantities given

$$\textit{No. of molecules reacted} = 0.002 \times 6.023 \times 10^{23}$$

$$\textit{No. of photons absorbed} = 3.0 \times 10^{16} \times 600$$

Substitution of values

$$\phi = \frac{0.002 \times 6.023 \times 10^{23}}{3.0 \times 10^{16} \times 600} = \mathbf{66.92}$$

SOLVED PROBLEM 20. 10% incident light is transmitted after passing through 2 cm thick glass. If glass is 1 cm thick, then how much light is absorbed of the same wavelength ?

SOLUTION :

Formula used

$$\log \frac{I}{I_o} = \frac{-kcx}{2.303}$$

Quantities given

$$\frac{I}{I_o} = 10\% = \frac{10}{100} = 0.1 \quad x = 2\text{ cm} \quad \text{(in first case)} \qquad x = 1\text{cm} \quad \text{(in second case)}$$

Substitution of values

$$\log 0.1 = -\frac{k \times c \times 2}{2.303} \qquad \text{...(i) for first case}$$

and

$$\log A = -\frac{k \times c \times 1}{2.303} \qquad \text{...(ii) for second case}$$

Dividing (i) by (ii) we get

$$\frac{\log 0.1}{\log A} = \frac{-k \times c \times 2}{2.303} \times \frac{2.303}{-k \times c \times 1}$$

$$\frac{\log 0.1}{\log A} = 2$$

or $$\log A = \frac{\log 0.1}{2}$$

$$= -0.5$$

$$A = \text{Antilog}(-0.5) = 0.3162$$

$$= 31.62\ \%$$

Thus the amount absorbed $= 100 - 31.62$

$$= \mathbf{68.38\ \%}$$

SOLVED PROBLEM 21. When irradiated with light of wavelength 5000 Å, 1×10^{-4} mole of a substance decomposed. How many photons are absorbed during the reaction if its quantum efficiency is 10.0 (Avogadro's number $= 6.02 \times 10^{23}$)

SOLUTION :

Formula used

$$\textit{Quantum yield, } \phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of photons absorbed}}$$

Quantities given

$\phi = 10.0$

No. of molecules reacted $= 1 \times 10^{-4} \times 6.02 \times 10^{23}$

Substitution of values

$$10.0 = \frac{1.0 \times 10^{-4} \times 6.02 \times 10^{23}}{\text{No. of photons absorbed}}$$

or $$\text{No. of photons absorbed} = \frac{1.0 \times 10^{-4} \times 6.02 \times 10^{23}}{10}$$

$$= \mathbf{6.02 \times 10^{18}}$$

SOLVED PROBLEM 22. If one mole of a compound absorbs light of wavelength 2537 Å, calculate the amount of energy absorbed in kilo joules per mole.

SOLUTION :

Formula used

$$\textit{Energy absorbed} = \frac{N\,h\,c}{\lambda}$$

Quantities given

$N = 6.02 \times 10^{23}$

$h = 6.62 \times 10^{-27}$ erg sec

$c = 3.0 \times 10^{10}$ cm sec^{-1}

$\lambda = 2537\ \text{Å} = 2537 \times 10^{-8}$ cm

Substitution of values

$$= \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{2537 \times 10^{-8}}$$

$$= 4.7125 \times 10^{12}\ \text{erg}$$

$$= 4.7125 \times 10^{5}\ \text{J}$$

$$= 4.7125 \times 10^{2}\ \text{kJ}$$

$$= \mathbf{471.25\ kJ}$$

SOLVED PROBLEM 23. On passing through 1 cm long in a solution of concentration of 10^{-3} M, the incident ray is 10% absorbed. What will be the concentration of the solution which absorbs 90% of incident of radiation in the same cell.

SOLUTION :

Formula used

$$\log \frac{I}{I_o} = \frac{-kcx}{2.303}$$

Quantities given

$I/I_o = 100 - 10 = 90\% = 0.9$ $c = 1 \times 10^{-3}$ M in first case

$I/I_o = 100 - 90 = 10\% = 0.1$ $c = ?$ in second case

Substitution of values

$$\log 0.9 = \frac{-k \times 1 \times 10^{-3} \times x}{2.303} \quad \text{....(i)} \quad \text{for first case}$$

$$\log 0.1 = \frac{-k \times c \times x}{2.303} \quad \text{...(ii)} \quad \text{for second case}$$

Dividing (i) by (ii) we get

$$\frac{\log 0.9}{\log 0.1} = \frac{-k \times 1 \times 10^{-3} \times x}{2.303} \times \frac{2.303}{-k \times c \times x}$$

$$\frac{-0.04575}{-1} = \frac{1 \times 10^{-3}}{c}$$

or
$$c = \frac{1 \times 10^{-3}}{0.04575}$$
$$= \mathbf{2.18 \times 10^{-2}\,M}$$

SOLVED PROBLEM 24. In the photochemical reaction between chlorine and hydrogen, 3×10^{-10} mole of chlorine have been converted into hydrochloric acid by irradiation with light of wavelength 3500Å. What is the quantum yield of the reaction if the light energy absorbed by the system is 7.16×10^{-15} kcal ?

SOLUTION : (i) To calculate the number of photons absorbed

Formula used

$$\textit{No. of photons absorbed} = \frac{\textit{Energy absorbed}}{\dfrac{hc}{\lambda}}$$

Quantities given

$$\textit{Energy absorbed} = 7.16 \times 10^{-15}\,\text{kcal} = 7.16 \times 10^{-15} \times 10^{3}\,\text{cal}$$
$$= 7.16 \times 10^{-15} \times 10^{3} \times 4.184 \times 10^{7}\,\text{erg}$$

$h = 6.62 \times 10^{-27}$ erg sec $c = 3 \times 10^{10}$ cm sec^{-1} $\lambda = 3500$ Å $= 3500 \times 10^{-8}$ cm

Substitution of values

$$\text{No. of photons absorbed} = \frac{7.16 \times 10^{-15} \times 10^{3} \times 4.184 \times 10^{7}}{\dfrac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{3500 \times 10^{-8}}}$$
$$= 5.28 \times 10^{7}$$

(ii) To calculate the quantum efficiency

$$\phi = \frac{\textit{No. of molecules } Cl_2 \textit{ reacted}}{\textit{No. of photons absorbed}}$$

Quantities given

No. of molecules of Cl_2 *reacted* $= 3 \times 10^{-10}$ mole

$= 3 \times 10^{-10} \times 6.02 \times 10^{23}$

No. of photons absorbed $= 5.28 \times 10^{7}$

Substitution of values

$$\phi = \frac{3 \times 10^{-10} \times 6.02 \times 10^{23}}{5.28 \times 10^{7}}$$

$$= \mathbf{3.42 \times 10^{6}}$$

SOLVED PROBLEM 25. Calculate the value of an einstein in kJ mol^{-1} for radiation of wavelength 4500 Å.

SOLUTION :

Formula used

$$E = \frac{N\,h\,c}{\lambda}$$

Quantities given

$N = 6.02 \times 10^{23}$

$c = 3 \times 10^{10}$ cm sec^{-1}

$h = 6.62 \times 10^{-27}$ erg sec

$\lambda = 4500$ Å $= 4500 \times 10^{-8}$ cm

Substitution of values

$$E = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{4500 \times 10^{-8}}$$

$$= 2.656 \times 10^{12} \text{ erg}$$

$$= \frac{2.656 \times 10^{12}}{10^{7}} \text{ J}$$

$$= \frac{2.656 \times 10^{12}}{10^{7} \times 10^{3}} \text{ kJ}$$

$$= \mathbf{265.68\ kJ}$$

SOLVED PROBLEM 26. Acetone can be photolysed by irradiating with light of $\lambda = 3100$ Å according to the reaction

$$(CH_3)_2CO \longrightarrow C_2H_6 + CO$$

In an experiment the vessel containing acetone absorbs 0.001 J per second and yields 3×10^{14} CO molecules per second. Calculate the quantum efficiency for the reaction.

SOLUTION :

Formula used

$$\phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of einsteins absorbed}}$$

Quantities given

No. of molecules of CO produced $= 3 \times 10^{14}$

$$\textit{No. of quanta absorbed} = \frac{\text{Total energy}}{\frac{h\,c}{\lambda}}$$

$$= \frac{0.001 \times 3100 \times 10^{-8}}{6.02 \times 10^{-27} \times 3 \times 10^{10}} \text{ J}$$

$$= \frac{0.001 \times 3100 \times 10^{-8} \times 10^{7}}{6.02 \times 10^{-27} \times 3 \times 10^{10}} \text{ erg}$$

$$= 1.56 \times 10^{15}$$

Substitution of values

$$\phi = \frac{3 \times 10^{14}}{1.56 \times 10^{15}}$$

$$= \mathbf{0.192}$$

SOLVED PROBLEM 27. In the photochemical reaction between Cl_2 and H_2, 2.5×10^{-10} mole of chlorine have been converted to hydrochloric acid by irradiation with light of 4500 Å. What is the quantum efficiency of the reaction if light absorbed in the system is 3.0×10^{-15} k J ?

SOLUTION : (i) To calculate the no. of photons absorbed

Formula used

$$\textit{No. of photons absorbed} = \frac{\textit{Total energy absorbed}}{\textit{Energy of a photon}}$$

Quantiti es given

$$\textit{Total energy absorbed} = 3.0 \times 10^{-15}$$

$$\textit{Energy of a photon} = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{4500 \times 10^{-8}}$$

$$= 4.41 \times 10^{-19} \text{ J}$$

Substitution of values

$$\text{No. of photons absorbed} = \frac{30 \times 10^{-15}\text{ J}}{4.41 \times 10^{-19}\text{ J}}$$

$$= 6.80 \times 10^{4}$$

(ii) To calculate the quantum efficiency

Formula used

$$\textit{Quantum efficiency} = \frac{\textit{No. of molecules reacted}}{\textit{No. of photons absorbed}}$$

Quantities given

$$\textit{No. of photons absorbed} = 6.80 \times 10^{4}$$

$$\textit{No. of molecules of } Cl_2 \textit{ reacted} = 2.50 \times 10^{-10} \times 6.02 \times 10^{23}$$

$$= 1.505 \times 10^{14}$$

Substitution of values

$$\text{Quantum efficiency} = \frac{1.505 \times 10^{14}}{6.80 \times 10^{4}}$$

$$= 2.213 \times 10^{9}$$

SOLVED PROBLEM 28. In the photochemical reaction

$$NH_{3\,(g)} \longrightarrow \tfrac{1}{2} N_{2\,(g)} + \tfrac{1}{2} H_{2\,(g)}$$

with light at wavelength 2100 Å it is found that 1940 J of energy decomposes 7.4×10^{-4} mole of NH_3. Calculate the quantum yield.

SOLUTION : (i) To calculate the energy of a photon

Formula used

$$E = \frac{hc}{\lambda}$$

Quantities given

$h = 6.62 \times 10^{-27}$ erg sec $\quad c = 3 \times 10^{10}$ cm sec^{-1} $\quad \lambda = 2100$ Å $= 2100 \times 10^{-8}$ cm

Substitution of values

$$E = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{2100 \times 10^{-8}}$$

$$= 9.457 \times 10^{-12} \text{ erg}$$

$$= 9.457 \times 10^{-19} \text{ J}$$

(ii) To calculate the quantum efficiency

Formula used

$$\phi = \frac{\textit{No. of molecules reacted}}{\textit{No. of photons absorbed}}$$

Quantities given

No. of the molecules reacted $= 7.4 \times 10^{-4}$ mole

$= 7.4 \times 10^{-4} \times 6.02 \times 10^{23}$ molecules

No. of photons absorbed $= \dfrac{\text{Energy absorbed}}{\text{Energy per photon}}$

$= \dfrac{1940\ \text{J}}{9.457 \times 10^{-19}\ \text{J}}$

$= 2.0485 \times 10^{21}$

Substitution of values

$$\phi = \frac{7.4 \times 10^{-4} \times 6.02 \times 10^{23}}{2.0485 \times 10^{21}}$$

$= \mathbf{0.217}$

ADDITIONAL PRACTICE PROBLEMS

1. In a certain experiment irradiation of biacetyl gas with UV radiations (2537 Å) for 5 hours produced 6.33 mole per litre of CO. The intensity of the radiation absorbed by acetyl gas was 1.71×10^{-6} J per second. Calculate the quantum yield of CO.

Answer. 0.97

2. Calculate percentage of light transmitted through 5 mm length of a liquid of absorption coefficient 2.5.

Answer. 28.65%

3. A 2 mm thick plate of a material transmits 70% of the incident light. Calculate the percentage of light transmitted if the thickness of the plate is 0.5 mm.

Answer. 91.47

4. Calculate the energy of one photon of light of wavelength 5000 Å. Will it be able to break a bond in a diatomic molecule which absorbs this photon and has a bond energy equal to 300 kJ mol^{-1} ?

Answer. 3.972×10^{-19} J ; No

5. Calculate the energy of a photon corresponding to wave length 360 nm. Given :
velocity of light = 3×10^{8} m sec^{-1}; $h = 6.62 \times 10^{-34}$ J sec^{-1}.

Answer. 5.525×10^{-19} J

6. A certain system absorbs 3×10^{16} quanta of light per second. Calculate the quantum efficiency of the process if 2.00×10^{-3} mole of the reactant was found to have reacted in 10 minutes.

Answer. 66.92

7. What percentage of light will be transmitted through two cells put together in the path of light, if their individual transmissions are 60% and 30%.

Answer. 18%

8. A system absorbs 9×10^{20} quanta of light per second. The number of moles of reactant decomposed in one second is 2.98×10^{-4}. Calculate the quantum efficiency of the system.

Answer. 0.2 molecule per quantum

9. A 0.55 mm thick glass is found to have a transmission of 70% for light of wavelength 2537 Å. What will be thickness of the glass if transmission is 40.7%.

Answer. 2.0 mm