

SECTION -III (CONDUCTION)

10. Electrolytic Conductance :

Specific Conductance

The resistance (R) of a metallic conductor is directly proportional to its length (l) and inversely proportional to its cross-sectional area (a), i.e.,

$$R \propto \frac{l}{a} \quad \Rightarrow \quad R = \rho \cdot \frac{l}{a}$$

$$\Rightarrow \quad \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a} \quad \dots\dots(1)$$

Where ρ is a constant depending upon the nature of the material and is called specific resistance of the material.

The reciprocal of the resistance is called conductance and similarly, the reciprocal of specific resistance is called specific conductance,

Thus, from equation (1)

$$\text{Specific conductance} = \text{observed conductance} \times \frac{l}{a} \quad \dots\dots(2)$$

When $l = 1 \text{ cm}$ and $a = 1 \text{ cm}^2$

Specific conductance = observed conductance

Thus, specific conductance is the conductance of a conductor which is observed when it is 1 cm in length and 1 sq. cm in cross-sectional area. In other words, it is the conductance of 1 cc of the conductor.

The unit of resistance is ohm (Ω) so unit of conductance will be ohm^{-1} , mho or Ω^{-1} and expressing l in cm and a in cm^2 , the unit of specific conductance will be $\text{ohm}^{-1}\text{cm}^{-1}$, $\Omega^{-1} \text{cm}^{-1}$ or mho cm^{-1} . In SI system, the units of specific conductance are Sm^{-1} where S stands for Siemen.

The equation (2) mentioned above is also applicable for solution of an electrolyte i.e. electrolytic conductor. The specific conductance of an electrolytic solution is defined as the conductance that is observed when two electrodes each of 1 sq. cm in cross-sectional area are dipped into solution at a distance of 1 cm apart. In other words, specific conductance is the conductance per c.c. solution of the electrolyte. It is denoted by the symbol κ (kappa). Sometimes κ_v or κ_c is also used, the subscript v or c standing for dilution or concentration, respectively, signifying that κ is dilution or concentration dependent.

Equivalent Conductance

Equivalent conductance is the conducting power of all the ions produced by one g-equivalent i.e. one equivalent of an electrolyte in a given solution. The equivalent conductance may, therefore, be defined as the conductance which is observed when two sufficiently large electrodes are dipped into solution at such a distance so as to enclose in between them the entire volume of solution containing one equivalent of the electrolyte. It is denoted by the symbol \wedge .

Let one equivalent of an electrolyte is dissolved in V mL solution. Then all the ions produced by 1 equivalent of the electrolyte will be present in this V mL solution. So, the conductance of this V c.c. solution will be the equivalent conductance of the electrolyte i.e.

$$\wedge_{\text{eq}} = \text{Conductance of } V \text{ c.c. solution containing one equivalent of the dissolved}$$

$$\begin{aligned}
 & \text{electrolyte.} \\
 & = \text{Conductance of 1 c.c solution} \times V \\
 & = \kappa \times V \quad \dots\dots(3a)
 \end{aligned}$$

Where v = volume of solution in c.c containing 1 equivalent of the electrolyte

If C be the normality of solution i.e. concentration of electrolytic solution in equivalent/L, then

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

$$\therefore \quad \Lambda = \frac{1000\kappa}{C} \quad \dots\dots(3b)$$

Unit of Λ : $\text{Ohm}^{-1} \text{cm}^{-1} \times \text{cm}^3$ i.e. $\text{Ohm}^{-1} \text{cm}^2$ or $\Omega^{-1} \text{cm}^2$

Molar Conductance

The recent trend is to describe electrolytic conductance in terms of molar conductance which is defined as the conductance of solution due to all the ions produced by one mole of the dissolved electrolyte in a given solution.

It is denoted by the symbol Λ_m

Λ_m and κ are inter-related as

$$\Lambda_m = \kappa \times v$$

$$\Rightarrow \quad \Lambda_m = \frac{1000\kappa}{C} \quad \dots\dots(4)$$

Where v = Volume of solution in c.c. containing one mole of the electrolyte and

C = Concentration of solution in mole L^{-1} i.e. molarity

The above inter-relationship may also be expressed as

Unit of Λ_m : $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

In SI system it is $\text{S m}^2 \text{mol}^{-1}$

Relation between Λ and Λ_m ;

$$\Lambda_m = n \text{ factor} \times \Lambda_{\text{eq}}$$

Where n = n-factor of the electrolyte = total charge carried by either ion = $\frac{M}{E}$

11. Variation of Conductance with Dilution :

Upon dilution i.e. lowering concentration, specific conductance decreases while equivalent and molar conductances increase. At infinite or almost zero concentration equivalent conductance and molar conductance attain their respective limiting values called equivalent conductance at infinite dilution (Λ^∞) or zero concentration (Λ^0) and molar conductance at infinite dilution (Λ_m^∞) or zero concentration (Λ_m^0), respectively. The increase of Λ_{eq} or Λ_m with dilution of a weak electrolyte is attributable to increase of degree of dissociation with dilution resulting into more number of ions in solution. Note that ions are carriers of electricity. The increase of Λ_{eq} and Λ_m of a strong electrolyte which remains completely ionised at all dilutions, is attributed to increase in the ionic mobilities of ions due to decrease in inter-ionic attraction. As dilution approaches infinity, the degree of dissociation of weak electrolyte approaches unity, the number of ions becomes maximum and hence Λ_{eq} as well as Λ_m approach their respective maximum value. In the case of strong electrolyte, however, the maximum value of Λ_{eq} or Λ_m is attained due to the maximum ionic mobilities of the ions since at infinite dilution the dissociation of strong electrolyte is complete and inter-ionic attraction ceases to exist completely.

The decrease in κ may also be explained in the following way: Upon dilution the number of ions, in the case of weak electrolyte, increases but volume of solution also increases. The increase of volume is in greater proportion than the increase of number of ions resulting into decrease in number of ions per c.c. solution. The specific conductivity being the conductivity of 1 c.c. solution, should obviously decrease.

The variation of molar conductance of a strong electrolyte with concentration is theoretically given by Debye-Hückel-Onsager equation:

$$\Lambda_m = \Lambda_m^0 - (A + B \Lambda_m^0) \sqrt{C}$$

Where A and B are the Debye-Hückel constants depending upon nature of the solvent and temperature and C is the molar concentration of solution.

For aqueous medium at 25°C:

$$\Lambda_m = \Lambda_m^0 - (60.2 + 0.229 \Lambda_m^0) \sqrt{C}$$

According to this equation a plot of Λ_m vs \sqrt{C} should be a straight line having the slope equal to $60.2 + 0.229 \Lambda_m^0$ and intercept equal to Λ_m^0 . This has been checked in the case of a number of uni-univalent electrolytes and found to be positive for $C \leq 0.02$ M. At higher concentration, the observed deviation from linearity is attributable to large inter-ionic attraction.

Determination of Conductance (κ , Λ_{eq} and Λ_m)

As already mentioned above

$$\kappa = \text{Observed conductivity} \times \frac{1}{a}$$

For a given conductivity cell in a given experiment, $\frac{1}{a} = \text{constant called cell constant (x)}$.

$$\text{Thus, } \kappa = \text{Observed conductance} \times x = \frac{1}{\text{Observed resistance}} \times x$$

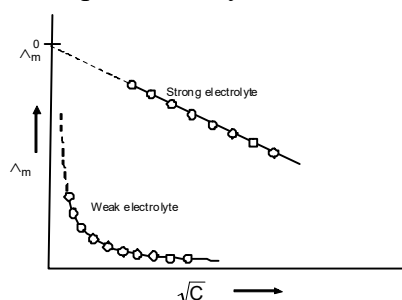
The resistance of a solution is determined by Wheatstone bridge method using a meter bridge the conductivity cell remains dipped in the test solution. The current used is AC.

The specific conductance of 0.1M KCl solution is known. The resistance of 0.1M KCl solution is first determined experimentally and thereby cell constant is calculated. The KCl solution is removed from the cell, it is washed with conductivity water and then filled with test solution. The resistance of the test solution is measured and since cell constant is already known so specific conductance of the test solution can be calculated.

From specific conductance, we determine Λ_{eq} and Λ_m using the equation (3) and equation (4) respectively.

Determination of Λ_m^0 or Λ^0

A plot of Λ_m vs \sqrt{C} as found experimentally is as shown below graphically.



The Λ_m vs \sqrt{C} plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, Λ_m values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

Λ_m values are then plotted against \sqrt{C} when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects Λ_m axis is Λ_m^0 of the strong electrolyte.

However, the plot in the case of weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to Λ_m axis. Hence extrapolation in this case is not possible. Thus, Λ_0 of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law to be discussed later.

Example 25.

1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

Solution :

Given $l = 2.1$ cm, $a = 4.2$ sq. cm, $R = 50$ ohm

Specific conductance, $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

$$\text{or } \kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductivity = $\kappa \times V$

$V =$ the volume containing 1 g equivalent = 1000 ml

$$\begin{aligned} \text{So } \text{Equivalent conductivity} &= 0.01 \times 1000 \\ &= 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1} \end{aligned}$$

Example 26.

Specific conductance of a decinormal solution of KCl is $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of a cell containing the solution was found to be 56. What is the cell constant?

Solution :

We know that

Sp. conductance = Cell constant \times conductance

$$\begin{aligned} \text{or } \text{Cell constant} &= \frac{\text{Sp. conductance}}{\text{Conductance}} \\ &= \text{Sp. conductance} \times \text{Resistance} \\ &= 0.0112 \times 56 \\ &= 0.6272 \text{ cm}^{-1} \end{aligned}$$

Example 27.

The specific conductivity of 0.02 M KCl solution at 25 °C is $2.768 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of this solution at 25 °C when measured with a particular cell was 250.2 ohms. The resistance of 0.01 M CuSO_4 solution at 25 °C measured with the same cell was 8331 ohms. Calculate the molar conductivity of the copper sulphate solution.

Solution :

$$\text{Cell constant} = \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}}$$

$$\begin{aligned}
 &= \frac{2.768 \times 10^{-3}}{1/250.2} \\
 &= 2.768 \times 10^{-3} \times 250.2
 \end{aligned}$$

For 0.01 M CuSO_4 solution

Sp. conductivity = Cell constant \times conductance

$$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

Molar conductance = Sp. cond. $\times \frac{1000}{C}$

$$\begin{aligned}
 &= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} \\
 &= 8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}
 \end{aligned}$$

Example 28.

A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of 4.5 cm² has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.

Solution :

Specific conductance = conductance \times cell constt.

$$\begin{aligned}
 K &= C \times \frac{l}{A} &= \frac{1}{R} \times \frac{l}{A} &= \frac{1}{250} \times \frac{1.72}{4.5} \\
 & &= 1.5288 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}
 \end{aligned}$$

$$\Lambda_e = K \times \frac{1000}{N} = 1.5288 \times 10^{-3} \times \frac{1000}{0.05} = 30.56 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

12. Kohlrausch's Law of Independent Migration of Ions :

Kohlrausch determined Λ_0 values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in Λ_0 values in each case remains the same .

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

He also determined Λ_0 values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in Λ_0 values in each case remains the same .

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions . Thus

$$\Lambda_m^0 = \lambda_+^0 + \lambda_-^0 \quad \dots\dots(5)$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation (5) is, however, correct only for binary electrolyte like NaCl, MgSO_4 etc.

For an electrolyte of the type of A_xB_y , we have :

$$\Lambda_m^0 = x\lambda_+^0 + y\lambda_-^0$$

Application of Kohlrausch's Law

(i) Determination of Λ_m^0 of a weak electrolyte :

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH , we determine experimentally Λ_m^0 values of the following three strong electrolytes :

- (a) A strong electrolyte containing same cation as in the test electrolyte, say HCl
- (b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa
- (c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH_3COOH is then given as :

$$\Lambda_m^0 (\text{CH}_3\text{COOH}) = \Lambda_m^0 (\text{HCl}) + \Lambda_m^0 (\text{CH}_3\text{COONa}) - \Lambda_m^0 (\text{NaCl})$$

Proof :

$$\Lambda_m^0 (\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \text{I}$$

$$\Lambda_m^0 (\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots \text{II}$$

$$\Lambda_m^0 (\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots \text{III}$$

Adding equation (I) and equation (II) and subtracting (III) from them :

$$\Lambda_{(\text{HCl})}^0 + \Lambda_{(\text{CH}_3\text{COONa})}^0 - \Lambda_{(\text{NaCl})}^0 = \lambda_{(\text{H}^+)}^0 + \lambda_{(\text{CH}_3\text{COO}^0)}^0 = \Lambda_{0(\text{CH}_3\text{COOH})}$$

(ii) Determination of degree of dissociation (α) :

$$\alpha = \frac{\text{No.. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

(iii) Determination of solubility of sparingly soluble salt :

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to Λ_m^0 as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\Lambda_m^0 = \frac{1000\kappa}{C},$$

Where C is the molarity of solution and hence the solubility.

(iv) Determination of ionic product of water :

From Kohlrausch's law, we determine Λ_m^0 of H_2O where Λ_m^0 is the molar conductance of water at infinite dilution when one mole of water is completely ionised to give one mole of H^+ and one mole of OH^- ions i.e.

$$\Lambda_m^0 (\text{H}_2\text{O}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{OH}^-}^0$$

Again using the following

$$\Lambda_m = \frac{\kappa \times 1000}{C}, \text{ where } C = \text{molar concentration i.e. mol L}^{-1} \text{ or mol dm}^{-3}$$

$$\Rightarrow \Lambda_m = \frac{\kappa}{C}, \text{ where } C = \text{concentration in mol m}^{-3}$$

Assuming that Λ_m differs very little from Λ_m^0

$$\Lambda_m^0 = \frac{\kappa}{C} \Rightarrow C = \frac{\kappa}{\Lambda_m^0}$$

Specific conductance (κ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation. K_w is then calculated as: $K_w = C^2$

Example 29.

The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm⁻¹ cm² equiv⁻¹, respectively at 25 °C. Calculate the equivalent conductance of acetic acid at infinite dilution.

Solution :

According to Kohlrausch's law,

$$\Lambda_{\infty \text{CH}_3\text{COONa}} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} = 91.0 \quad \text{.....(i)}$$

$$\Lambda_{\infty \text{HCl}} = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} = 426.16 \quad \text{.....(ii)}$$

$$\Lambda_{\infty \text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 126.45 \quad \text{.....(iii)}$$

Adding equations (i) and (ii) and subtracting (iii),

$$\begin{aligned} \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} + \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} - \lambda_{\text{Na}^+} - \lambda_{\text{Cl}^-} \\ = 91.0 + 426.16 - 126.45 \end{aligned}$$

$$\lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} = \Lambda_{\infty \text{CH}_3\text{COOH}} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

Example 30.

A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductance of Na⁺ and Cl⁻ ions at the same temperature are 43.0 and 65.0 ohm⁻¹ respectively, calculate the degree of dissociation of NaCl solution.

Solution :

Equivalent conductance of N/10 NaCl solution

$$\begin{aligned} \Lambda_v &= \text{Sp. conductivity} \times \text{dilution} \\ &= 0.0092 \times 10000 \\ &= 92 \text{ ohm}^{-1} \end{aligned}$$

$$\begin{aligned} \Lambda_{\infty} &= \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} \\ &= 43.0 + 65.0 = 108 \text{ ohm}^{-1} \end{aligned}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_{\infty}} = \frac{92}{108} = 0.85$$

Example 31.

The specific conductivity of a saturated solution of silver chloride is $2.30 \times 10^{-6} \text{ mho cm}^{-1}$ at 25°C . Calculate the solubility of silver chloride at 25°C ;

if $\lambda_{\text{Ag}^+} = 61.9 \text{ mho cm}^2 \text{ mol}^{-1}$ and $\lambda_{\text{Cl}^-} = 76.3 \text{ mho cm}^2 \text{ mol}^{-1}$.

Solution :

Let the solubility of AgCl be s gram mole per litre

$$\text{Dilution} = \frac{1000}{s}$$

$$\begin{aligned}\Lambda_{\infty \text{AgCl}} &= \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-} \\ &= 61.9 + 76.3 \\ &= 138.2 \text{ mho cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\text{Sp. conductivity} \times \text{dilution} = \Lambda_{\infty \text{AgCl}} = 138.2$$

$$2.30 \times 10^{-6} \times \frac{1000}{s} = 138.2$$

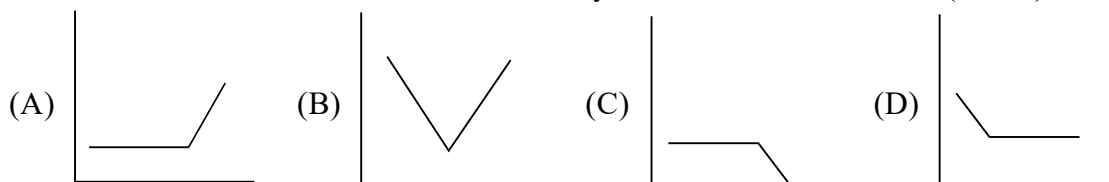
$$\begin{aligned}s &= \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mole per litre} \\ &= 1.66 \times 10^{-5} \times 143.5 \text{ gL}^{-1} \\ &= 2.382 \times 10^{-3} \text{ gL}^{-1}\end{aligned}$$

6. Daily Practice Problem Sheet

Conductance (Objective Questions)

- Q.1** The specific conductance of 0.01 M solution of KCl is $0.0014 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C . Its equivalent conductance is :
(A) 14 (B) 140 (C) 1.4 (D) 0.14
- Q.2** The equivalent conductivity of 0.1 N CH_3COOH at 25°C is 80 and at infinite dilution 400 ohm^{-1} . The degree of dissociation of CH_3COOH is :
(A) 1 (B) 0.2 (C) 0.1 (D) 0.5
- Q.3** The equivalent conductance at infinite dilution of NaCl, HCl and CH_3COONa at 298 K are 126.0, 426.0 and $91.0 \text{ ohm}^{-1} \text{ cm}^2$ respectively. The value of equivalent conductance of acetic acid at infinite dilution at the same temperature is :
(A) 644.0 (B) 300.0 (C) 517.0 (D) 391.0
- Q.4** The specific conductance of a salt of 0.01M concentration is 1.061×10^{-4} . Molar conductance of the same solution will be :
(A) 1.061×10^{-4} (B) 1.061 (C) 10.61 (D) 106.1
- Q.5** At infinite dilution of an electrolyte, the equivalent conductances of cations and anions are :
(A) independent of each other (B) interdependent of each other
(C) dependent on solvent molecules (D) dependent on charge carried by ions
- Q.6** The specific conductances of a 0.1 N KCl solution at 23°C is $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of the cell containing solution at the same temperature was found to be 55 ohm. The cell constant will be :
(A) 0.142 cm^{-1} (B) 0.918 cm^{-1} (C) 1.12 cm^{-1} (D) 0.616 cm^{-1}
- Q.7** The conductivity of 0.01 mol/dm^3 aqueous acetic acid at 300 K is $19.5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ and the limiting molar conductivity of acetic acid at the same temperature is $390 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The degree of dissociation of acetic acid is :
(A) 0.5 (B) 0.05 (C) 5×10^{-3} (D) 5×10^{-7}
- Q.8** The ionization constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is $19.6 \text{ S cm}^2 \text{ eq}^{-1}$. The equivalent conductance of the electrolyte at infinite dilution (in $\text{S cm}^2 \text{ eq}^{-1}$) will be :
(A) 250 (B) 196 (C) 392 (D) 384
- Q.9** The resistance of 1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15 cm^{-1} . The equivalent conductance (in $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$) of 1 N acetic acid is :
(A) 4.6 (B) 9.2 (C) 18.4 (D) 0.023
- Q.10** The cell constant of a given cell is 0.47 cm^{-1} . The resistance of a solution placed in this cell is measured to be 31.6 ohm. The conductivity of the solution (in S cm^{-1} where S has usual meaning) is :
(A) 0.15 (B) 1.5 (C) 0.015 (D) 150
- Q.11** If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4 cm^{-1} then its molar conductance in $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ will be :
(A) 10^4 (B) 10^3 (C) 10^2 (D) 10
- Q.12** Which of the following solutions of KCl has the lowest value of specific conductance ?
(A) 1M (B) 0.1 M (C) 0.01 M (D) 0.001 M
- Q.13** Which of the following solutions of KCl has lowest value of equivalent conductance ?
(A) 1M (B) 0.1M (C) 0.01 M (D) 0.001 M

- Q.14** Under which of the following conditions, conductance, sp conductance and eq. conductance are all equal ?
 (A) 1000 cc of solution contains 1 eq. of electrolyte
 (B) 100 cc of solution contains 1 eq. of electrolyte
 (C) 10 cc of solution contains 1 eq. of electrolyte
 (D) 1 cc of solution contains 1 eq. of electrolyte
- Q.15** If V , in the equation $\Lambda = \text{sp. cond} \times V$, is the volume in cc containing 1 eq. of the electrolyte ; V for a N/10 solution will be :
 (A) 10 cc (B) 100 cc (C) 1000 cc (D) 10,000 cc
- Q.16** At infinite dilution, the eq. conductances of CH_3COONa , HCl and CH_3COOH are 91, 426 and 391 mho cm^2 respectively at 25 °C. The eq. conductance of NaCl at infinite dilution will be :
 (A) 126 (B) 209 (C) 391 (D) 908
- Q.17** $\lambda_{\text{CH}_3\text{COOH}} = 20 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ and $\lambda_{\text{CH}_3\text{COOH}}^\infty = 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$, then pH of 1 M CH_3COOH solution is :
 (A) 1.3 (B) 0 (C) 1.7 (D) 4
- Q.18** The equivalent conductivity of 0.1 M weak acid is 100 times less than that at infinite dilution. The degree of dissociation is :
 (A) 100 (B) 10 (C) 0.01 (D) 0.001
- Q.19** Molar ionic conductivities of a bivalent electrolyte are 57 and 73. The molar conductivity of the solution will be :
 (A) 130 $\text{S cm}^2 \text{ mol}^{-1}$ (B) 65 $\text{S cm}^2 \text{ mol}^{-1}$ (C) 260 $\text{S cm}^2 \text{ mol}^{-1}$ (D) 187 $\text{S cm}^2 \text{ mol}^{-1}$
- Q.20** The conductivity of the saturated solution of some bivalent salt XY is $3.06 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ and its equivalent conductivity is $1.53 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$. The value of K_{sp} of XY is :
 (A) 4×10^{-6} (B) 2.5×10^{-9} (C) 2.5×10^{-13} (D) 1×10^{-6}
- Q.21** The conductivity of 0.25 M solution of univalent weak electrolyte XY is $0.0125 \Omega^{-1} \text{ cm}^{-1}$. The value of Λ_m^∞ of XY is $500 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. the value of Ostwald dilution constant of AB is :
 (A) 2.5×10^{-3} (B) 2.5×10^{-4} (C) 2.8×10^{-3} (D) 2.8×10^{-4}
- Q.22** Equivalent conductance at infinite dilution of BaCl_2 , H_2SO_4 and HCl aq. solutions are x_1 , x_2 and x_3 respectively. Equivalent conductance of BaSO_4 solution is :
 (A) $x_1 + x_2 - x_3$ (B) $x_1 - x_2 - x_3$ (C) $x_1 + x_2 - 2x_3$ (D) $x_1 - 2x_2 + x_3$
- Q.23** CH_3COOH is titrated with NaOH solution. Which is true statement ?
 (A) conductance decreases upto equivalence point, after which it increases
 (B) conductance increases upto equivalence point, after which it decreases
 (C) conductance first increases (but not rapidly) upto equivalence point and then increases rapidly after equivalence point
 (D) none of these
- Q.24** If molar conductance at infinite dilution of $(\text{NH}_4)_2\text{SO}_4$, NaOH and Na_2SO_4 solutions are x_1 , x_2 and x_3 respectively, then molar conductance of NH_4OH solution is -
 (A) $\frac{x_1 + 2x_2 - x_3}{2}$ (B) $x_1 + 2x_2 - x_3$ (C) $\frac{x_1 + x_2 - x_3}{2}$ (D) $x_1 + x_2 - x_3$
- Q.25** If NaOH with HCl , variation of conductance y-axis with addition of HCl (x-axis) will be :



SOLVED PROBLEMS

SUBJECTIVE

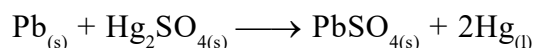
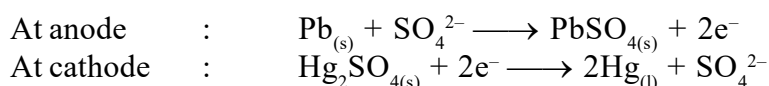
Problem 1.

Consider the cell : $Pb | PbSO_4 | Na_2SO_4 \cdot 10H_2O || Hg_2SO_4 | Hg$

The temperature coefficient of the emf of above cell is $0.000174V\ deg^{-1}$ and heat of reaction is $-176.146\ kJ$. Calculate emf of the cell .

Solution :

The cell reaction is :

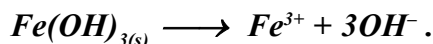


i.e. the number of electrons involved are two, substituting the values of known terms in equation (3)

$$\begin{aligned} -176146\ J &= -(2)(96500\ J\ V^{-1})E^0 + (298\ K)(96500\ J\ V^{-1})(2)(0.00174\ VK^{-1}) \\ E^0 &= 0.9645V \end{aligned}$$

Problem 2.

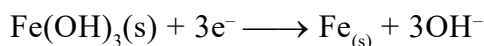
The solubility product of $Fe(OH)_3$ at $25\ ^\circ C$ is $10^{-36.4}$ and $E^0(Fe^{3+}/Fe) = -0.036\ V$. Calculate the standard emf of the reaction ,



Solution :

The cell can be formed as : $Fe | Fe^{3+} || OH^- | Fe(OH)_{3(s)} | Fe$

The electrode reactions can be written as : $Fe_{(s)} \longrightarrow Fe^{3+} + 3e^-$



Overall reaction is i.e., by adding

$$\text{i.e. } E^0 = E_{OH^-/Fe(OH)_3/Fe}^0 - E_{Fe^{2+}/Fe}^0$$

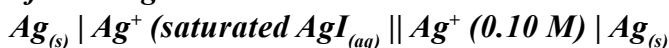
$E_{OH^-/Fe(OH)_3/Fe}^0$ can be calculated if we know E^0 and E^0 can be calculated as follows

$$E^0 = \frac{0.0591}{0.3} \log 10^{-36.4} = \frac{0.0591 \times (-36.4)}{3} = -0.75V$$

$$E_{OH^-/Fe(OH)_3/Fe}^0 = -0.75 - 0.036 = -0.786V$$

Problem 3.

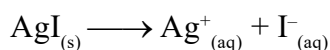
For the following cell :



$E_{cell} = 0.417$. Calculate K_{sp} of AgI

$$E_{Ag^+/Ag}^0 = 0.80V$$

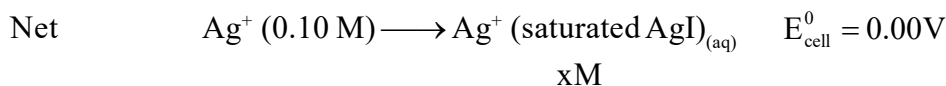
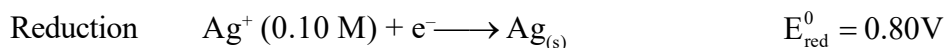
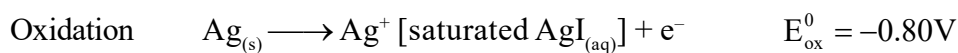
Solution :



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

$$\text{Since } [Ag^+] = [I^-] \quad \therefore K_{sp} = [Ag^+]^2$$

If we manage to calculate $[Ag^+]$ in saturated in L.H.S. oxidation half cell (anode), then K_{sp} can be calculated.



$$K = \left(\frac{x}{0.1} \right)$$

$$E_{cell} = 0.417V \text{ (given)}$$

Using Nernst equation $E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log K$

$$0.417 = 0.00 - \frac{0.0591}{1} \log \left(\frac{x}{0.1} \right)$$

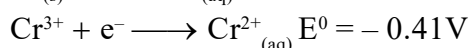
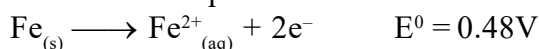
$$\log \left(\frac{x}{0.1} \right) = \frac{0.417}{0.0591} = -7.0558$$

$$x = [Ag^+] \text{ in saturated } AgI = 8.79 \times 10^{-9}$$

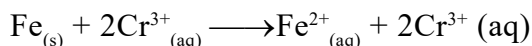
$$K_{sp} = [Ag^+]^2 = (8.79 \times 10^{-9})^2 = 7.73 \times 10^{-17}$$

Problem 4.

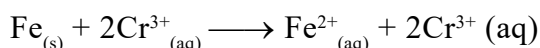
The standard electrode potential are for the following reactions :



If the excess of $Fe_{(s)}$ is added to a solution in which $[Cr^{3+}] = 1 \text{ M}$, what will be $[Fe^{2+}]$ when equilibrium is established at 298K ?

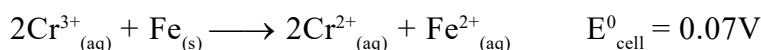
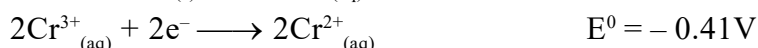
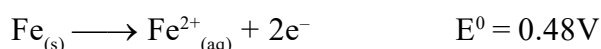


Solution :



$$K = \frac{[Fe^{2+}][Cr^{2+}]^2}{[Cr^{3+}]^2}$$

$$K = \frac{x(2x)^2}{[Cr^{3+}]^2} = \frac{4x^3}{(1-2x)^2} \quad x < 0.5$$



When equilibrium is attained $E_{cell} = 0$

By Nernst equation $E_{cell} = E_{cell}^0 - \frac{0.0691}{2} \log K$

$$E_{\text{cell}}^0 = \frac{0.0591}{2} \log K \quad \log K = \frac{0.07 \times 2}{0.0591} = 2.3689$$

$$K = \frac{4x^3}{(1-2x)^2} = 23.81$$

It will be tedious and time consuming to calculate x from cubic equation.

Also $x < 0.5$ and x can't be neglected since value of K is high.

The best way is to select range of value of x.

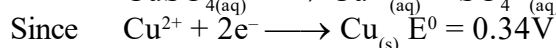
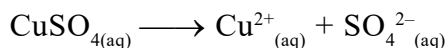
Start with values of $x < 0.5$

Problem 5.

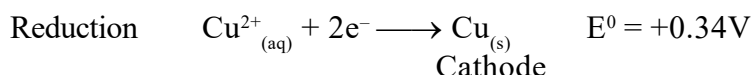
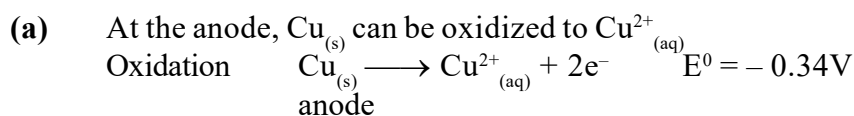
CuSO₄ solution is electrolyzed. Predict the electrode reactions and the net electrolysis reaction when the anode is made of (a) copper and (b) platinum. Also calculate E_{cell}^0 of each case.

Solution :

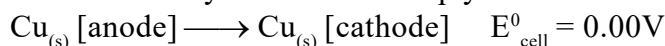
We refer E^0 values of different reactions from E.C.S.



Hence in both cases the reduction of $\text{Cu}^{2+}_{(\text{aq})}$ to $\text{Cu}_{(\text{s})}$ seems quite feasible.



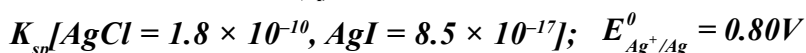
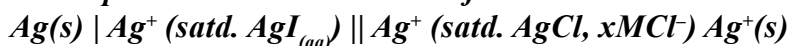
The net electrolysis reaction is simply



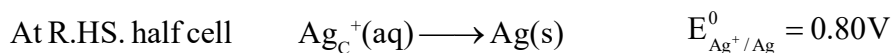
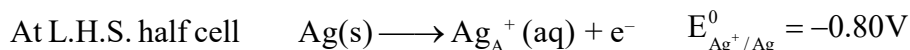
Only a slight voltage

Problem 6.

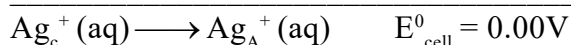
It is desired to construct the following voltaic cell to have $E_{\text{cell}} = 0.0860\text{V}$. What $[\text{Cl}^-]$ must be present in the cathode half cell to achieve this result?



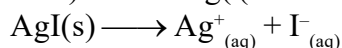
Solution :



R.H.S.



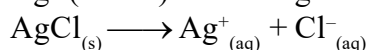
Ag^+ (L.H.S.) is from $\text{Ag}(\text{satd. AgI})$



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

$$[\text{Ag}^+]_{\text{AgI}} = [\text{Ag}^+]_{\text{A}} = \sqrt{K_{\text{sp}}} = \sqrt{8.5 \times 10^{-17}} = 0.9220 \times 10^{-8}\text{M}$$

Ag^+ (R.H.S.) is from AgCl in presence of $[\text{Cl}^-] = x\text{M}$



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

$$[Ag^+]_C = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-8}}{x}$$

$$[Cl^-]$$

$$E_{cell} = E_{cell}^0 = \frac{0.0591}{1} \log \frac{[Ag^+]_A}{[Ag^+]_C}$$

$$0.0860 = -0.0591 \log \frac{0.9220x \times 10^{-8}}{1.8 \times 10^{-10}} - \frac{0.0860}{0.0591} = \log 51.22x$$

$$-1.4562 = \log 51.22 + \log x = 1.7095 + \log x$$

$$\log x = -3.1647$$

$$x = 7 \times 10^{-4} M$$

$$[Cl^-] = 7 \times 10^{-4} M$$

Problem 7.

The emf of the cell is 0.788V

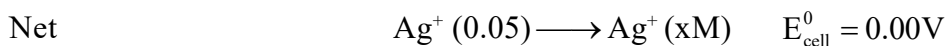
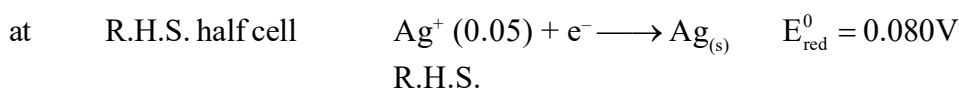
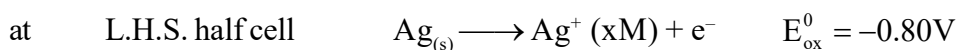


Calculate the solubility product of AgI. $E_{Ag^+/Ag}^0 = 0.80V$

Solution :

KI is strong electrolyte, hence, $[I^-]_{L.H.S.} = 0.05 M$

AgI_(s) is sparingly soluble. If we manage to calculate Ag⁺ (Ag) in L.H.S., half cell, K_{sp} can be calculated.



$$K = \frac{[Ag^+]_{L.H.S.}}{[Ag^+]_{R.H.S.}} = \frac{x}{0.05}$$

$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log K \Rightarrow 0.788 = 0 - \frac{0.0591}{1} \log \left(\frac{x}{0.05} \right)$$

$$\log \left(\frac{x}{0.05} \right) = -13.3333 = 14.66671$$

$$\frac{x}{0.05} = 4.6416 \times 10^{-14}; x = 2.231 \times 10^{-15}$$

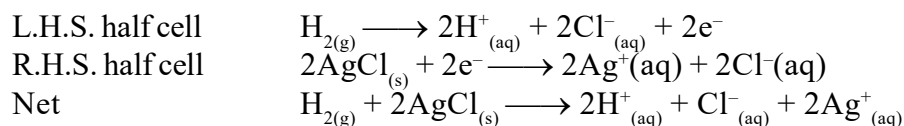
$$[Ag^+]_{L.H.S.} = 2.31 \times 10^{-15} M$$

$$[I^-]_{L.H.S.} = 0.05 M$$

$$K_{sp} = [Ag^+][I^-] = 2.31 \times 10^{-15} \times 0.05 = 1.16 \times 10^{-16}$$

Problem 8.

The emf of the following cell 0.265V at 25°C and 0.2595V at 35°C. Calculate heat of reaction taking place at 25°C. $Pt(H_2) | HCl(aq) || AgCl | Ag$

Solution :

$$\Delta H \text{ (heat of reaction)} = nF \left[T \left(\frac{dE}{dT} \right) - E \right]$$

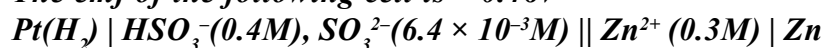
$$\frac{dE}{dT} = \frac{0.2595 - 0.265}{308 - 298} = 5.5 \times 10^{-4}$$

$$n = 2, F = 96500 \text{ C}, E = 0.265 \text{ V at } 298 \text{ K}$$

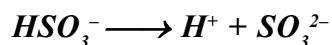
$$= -82777.7 \text{ J} = -82.8 \text{ kJ}$$

Problem 9.

The emf of the following cell is -0.46 V



If $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$, calculate pK_a of HSO_3^- i.e. for the equilibrium

**Solution:**

Half cell	Reaction	E^0
L.H.S.	$\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$	$E_{\text{ox}}^0 = 0.00 \text{ V}$
R.H.S.	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	$E_{\text{cell}}^0 = 0.76 \text{ V}$
Net	$\text{Zn}^{2+} + \text{H}_2 \longrightarrow \text{Zn} + 2\text{H}^+$	$E_{\text{cell}}^0 = 0.76 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K$$

$$-0.46 = -0.76 - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{(0.3)}$$

$$[\text{H}^+] = 4.60 \times 10^{-6} \text{ M}$$



$$K = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = \frac{4.6 \times 10^{-6} \times 6.4 \times 10^{-3}}{0.4} = 7.36 \times 10^{-8}$$

$$pK_a = 7.13$$

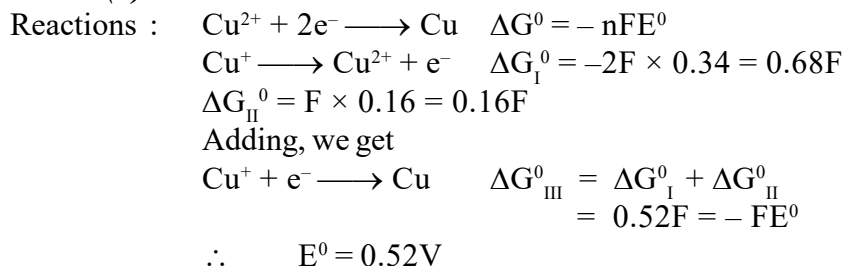
OBJECTIVE

Problem 1.

The standard oxidation potentials of Cu/Cu^{2+} and $\text{Cu}^+/\text{Cu}^{2+}$ are -0.4V and -0.16V respectively. The standard electrode potential of Cu^+/Cu would be :

- (a) $0.18V$ (b) $0.52V$ (c) $0.82V$ (d) $0.49V$

Solution : (b)

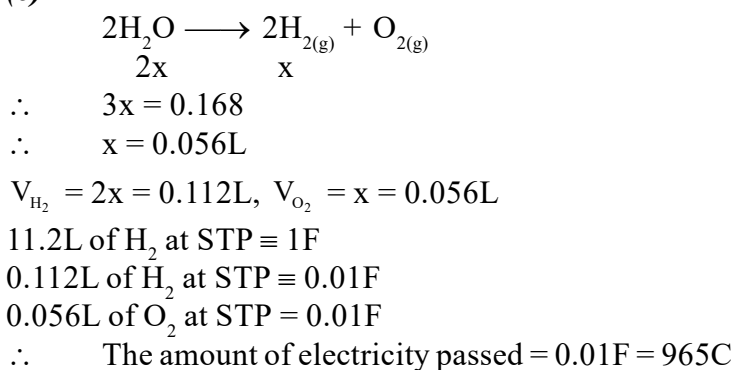


Problem 2.

Acidified water is electrolysed using an inert electrode. The volume of gases liberated at STP is 0.168L. The quantity of charge passed through the acidified water would be :

- (a) $96,500C$ (b) $9,650C$ (c) $965C$ (d) $168C$

Solution : (c)



Problem 3.

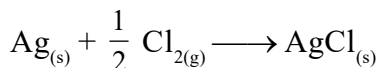
The useful work done during the reaction $\text{Ag}_{(\text{s})} + \frac{1}{2} \text{Cl}_{2(\text{g})} \longrightarrow \text{AgCl}_{(\text{s})}$ would be

- (a) 110 kJ mol^{-1} (b) 220 kJ mol^{-1} (c) 55 kJ mol^{-1} (d) 100 kJ mol^{-1}

Given $E_{Cl_2/Cl^-}^0 = 1.36V, E_{AgCl/Ag/Cl^-}^0 = 0.220V$, $P_{Cl_2} = 1 \text{ atm}$ and $T = 298K$

Solution : (a)

For the cell reaction



$$E^0 = -1.14V \quad \text{or} \quad E = E^0 - \frac{0.0592}{1} \log P_{\text{Cl}_2}^{1/2}$$

Under standard conditions, $P_{\text{Cl}_2} = 0$

$$\therefore \log P_{Cl_2}^{1/2} = 0$$

$$\therefore \text{Useful work} = -W_{\max} = -nFE = (-1) \times (-1.14) \times 96500 \times 10^{-3} \text{ kJ} = 110 \text{ kJ mol}^{-1}$$

Problem 4.

A current of 0.250 A is passed through 400 ml of a 2.0 M solution of NaCl for 35 minutes. What will be the pH of the solution after the current is turned off?

- (a) 12.98 (b) 12.13 (c) 10.48 (d) 9.24

Solution : (b)

After electrolysis aqueous NaCl is converted into aqueous NaOH.

$$\begin{aligned}\text{The quantity of electricity passed} &= \frac{0.250 \times 35 \times 60}{96500} \text{ F} \\ &= 5.44 \times 10^{-3} \text{ F}\end{aligned}$$

The number of equivalents of OH^- ion formed = 5.44×10^{-3}

$$\therefore \text{Molarity of NaOH} = \frac{5.44 \times 10^{-3}}{0.4 \text{ L}} = 1.36 \times 10^{-2}$$

$$\therefore \text{pOH} = -\log (1.36 \times 10^{-2}) = 1.87$$

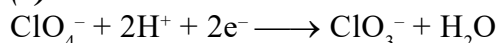
$$\therefore \text{pH} = 12.13$$

Problem 5.

How much charge should be supplied to a cell for the electrolytic production of 245 gm NaClO_4 from NaClO_3 if the anode efficiency for the required reaction is 60%?

- (a) $6.43 \times 10^5 \text{ C}$ (b) 6.67F (c) 6.43×10^6 (d) 66.67F

Solution : (a)



$$\text{Number of equivalents of NaClO}_4 = \frac{245}{61.25} = 4 = 4\text{F}$$

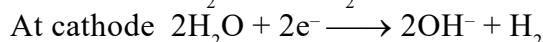
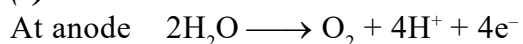
$$\text{No. of Faradays} = \frac{4 \times 100}{60} = 6.67\text{F} = 6.43 \times 10^5 \text{ C}$$

Problem 6.

The volume of gases liberated at STP when a charge of 2F is passed through aqueous solution of sodium phosphate, is :

- (a) 11.2L (b) 44.8L (c) 33.6L (d) 22.4L

Solution : (c)



After passage of 2F, one mole of H_2 and 1/2 mole of O_2 would be produced. The total volume is 33.6L.

Problem 7.

Specific conductance of 0.01 M KCl solution is $x \text{ ohm}^{-1} \text{ cm}^{-1}$. When conductivity cell is filled with 0.01 M KCl the conductance observed is $y \text{ ohm}^{-1}$. When the same cell is filled with 0.01 M H_2SO_4 , the observed conductance was $Z \text{ ohm}^{-1} \text{ cm}^{-1}$. Hence specific conductance of 0.01 M H_2SO_4 is :

- (a) xz (b) $\frac{z}{xy}$ (c) $\frac{xz}{y}$ (d) $\frac{xy}{z}$

Solution : (c)

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}} = \frac{x}{y} \text{ cm}^{-1}$$

Specific conductance of 0.01 M H_2SO_4

$$= \text{Observed conductance} \times \text{Cell constant} = z \times \frac{x}{y} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Problem 8.

Among the cation H^+ , Li^+ , Na^+ and K^+ , the one with highest ionic mobility and another with lowest ionic mobility respectively are :

- (a) $[H^+, K^+]$ (b) $[K^+, H^+]$ (c) $[Li^+, Na^+]$ (d) $[H^+, Li^+]$

Solution : (d)

H^+ ion has the maximum ionic mobility which is explainable by Grothus mechanics, Li^+ having the maximum charge density, is the most hydrated ion among the lot and hence the lowest ionic mobility.

Problem 9.

The specific conductance has the unit :

- (a) $ohm^{-1} cm^{-1}$ (b) $ohm.cm$ (c) $ohm cm^{-1}$ (d) $ohm^{-1}.cm$

Solution : (a)

$$\text{Specific conductance} = \text{Observed conductance} \times \frac{\lambda}{a}$$

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

6. Daily Practice Problem Sheet

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. B | 2. B | 3. D | 4. C | 5. A | 6. D | 7. B |
| 8. C | 9. A | 10. C | 11. B | 12. D | 13. A | 14. D |
| 15. D | 16. A | 17. A | 18. C | 19. A | 20. D | 21. A |
| 22. C | 23. C | 24. A | 25. B | | | |