CHAPTER / 03

Electrochemistry

Topics Covered

Conductor, Electrolytes and their Dissociation, Electrolysis and Its Law and Applications

- Conductors
- Electrolytes and Non-electrolytes
- Arrhenius Theory of Electrolytic Dissociation
- Electrolysis
- Faraday's Law of Electrolysis
- Conductance and Resistance
- Kohlrausch's Law

Electrochemical Cells and Series, Nernst Equation, Batteries and Corrosion

- Galvanic Cells
- Electrode Potential
- Nernst Equation
- Electromotive Force of Simple Cells
- Electrochemical Series
- Electrochemical cell and Gibbs Energy of the Reaction
- Batteries
- Corrosion

TOPIC ~01 Conductor, Electrolytes and their Dissociation, Electrolysis and Its Law and Applications

Electrochemistry is the study of production of electricity from energy which is released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations. A chemical reaction in which electrons are lost by one substance and gained by another is called **redox reaction**. In this, transfer of electrons is the reason for electric current.

Conductors

The substances which have very large values of conductivity are known as conductors, e.g. metals and their alloys, certain non-metals like carbon-black, graphite and some organic polymers are electronically conducting. Conductors are of the following types :

(i) **Metallic conductors** In metallic conductors, the flow of electricity takes place due to the flow of electrons only, i.e. no flow of matter takes place. Thus, the matter does not decompose. Due to the vibration of Kernels, the electrical conduction decreases with decrease in temperature.

(ii) **Electrolytic conductors or electrolytes** In electrolytic conductors, the flow of electricity takes place due to the flow of charge, i.e. matter decomposes into ions. The electrical conduction increases with increase of temperature due to increase in dissociation.

(iii) **Semiconductors** The substances which have conductivity between that of conductors and insulators are known as semiconductors, e.g. silicon, doped silicon and gallium arsenide.

(iv) **Superconductors** The substances which have zero resistivity or infinite conductivity, are known as superconductors,

e.g. metals and their alloys at very low temperatures (0 to 15 K). Now-a-days, a number of ceramic materials and mixed oxides show superconductivity at temperatures as high as 150 K.

Difference between Metallic and Electrolytic Conduction

Metallic Conduction

- This conduction occurs due to flow of electrons.
- It does not involve transfer of matter.
- There is no change in the chemical properties of the conductor.
- With the increase in temperature, metallic conduction shows an increase in resistance.

Electrolytic Conduction

- This conduction occurs due to the movement of ions in solution or in a fused electrolyte.
- It involves transfer of matter in the form of ions.
- There is a change in the chemical properties of conductor as it involves chemical reactions at the electrodes.
- With the increase in temperature, electrolytic conduction shows a decrease in resistance.

Electrolytes and Non-electrolytes

Electrolytes

The solutes which dissociate into ions when dissolved in water, are called electrolytes. These form a solution, which conducts electricity.

However, not all the electrolytes ionise to the same extent in solution. Depending upon the extent of ionisation, the electrolytes are divided into two classes :

(i) **Strong electrolytes** The electrolytes which dissociate completely into ions in solution are called strong electrolytes, e.g. NaCl, NaOH etc. Strong electrolytes practically dissociate completely at all concentrations.

(ii) **Weak electrolytes** The electrolytes which do not ionise completely in aqueous as well as in molten state are called weak electrolytes, e.g. H_2CO_3, CH_3COOH etc.

A weak electrolyte (like acetic acid) does not dissociate completely at all concentrations.

Non-electrolytes

A solution of solute like urea, glucose, etc., does not contain any ion, hence the solution is a poor conductor of electricity. Such solutes are termed as non-electrolytes.

Arrhenius Theory of Electrolytic Dissociation

This theory explains the mechanism of electrolysis and abnormal behaviour of electrolytes in dilute solutions.

The main postulates of this theory are:

(i) In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation into positive and negative ions. The positively charged ions are called **cations** and the negatively charged ions are called **anions.**

(ii) When a current of electricity is passed through a solution of an electrolyte, the positively charged ions move towards cathode and negatively charged ions move towards anode. They ultimately lose their charges and convert into products. This movement of ions constitutes the electric current in the solution.

(iii) A dynamic equilibrium, called the **ionic equilibrium,** is established between the ions and undissociated molecules.

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

(iv) The properties of solutions of electrolytes are essentially the properties of individual ions.

(v) The fraction of the total number of molecules undergoing dissociation is called the **degree of dissociation** (α). Alternatively, the fraction of the amount of the electrolyte in solution present as free ions is called the degree of dissociation.

$$\alpha = \frac{\text{Number of molecules of electrolyte dissociated as ions}}{\text{Total number of molecules of electrolyte dissolved}}$$

$$\text{or} \quad \alpha = \frac{\text{Amount of electrolyte dissociated}}{\text{Initial amount}}$$

Degree of dissociation (α) increases with dilution and reaches to the maximum limit (unity) at infinite dilution for weak electrolytes.

Electrolysis

The cell which converts electrical energy to chemical energy are called **electrolytic cells**. In this oxidation occurs at anode and it is a positive plate while reduction occurs at cathode and it is a negative plate. In electrolytic cells, electrical energy is used to carry out non-spontaneous chemical reactions and the **process** which takes place in an electrolytic cell is called **electrolysis**.

Many metals, e.g. Na, Mg, Al, etc., are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose.

Faraday's Laws of Electrolysis

The quantitative aspect of electrolysis was studied extensively by Michael Faraday and his laws of electrolysis are known as Faraday's laws of electrolysis.

Faraday's First Law

The amount of chemical reaction which occurs at any electrode during electrolysis by passing current is proportional to the quantity of electricity passing through the electrolyte (in solution or in molten state).

Thus, w g of the substance gets deposit on passing Q coulomb of electricity

$$w \propto Q \quad \text{or } w = ZQ \ \text{ or } \ w = Zit$$

where, Q = quantity of electricity, i = current (in A) t = time (in s), Z = constant of proportionality called electrochemical equivalent.

Faraday's Second Law

The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights,

i.e. $$\frac{w_1}{E_1} = \frac{w_2}{E_2} = \frac{w_3}{E_3} \dots\dots\dots$$

where, w_1 is the mass of substance deposited and E_1 is its equivalent weight and so on.

Faraday's Constant

It is defined as the amount of substance liberated at the electrode when current of one ampere is passed through the electrolyte for one second. Its value is $96500\,\text{C mol}^{-1}$.

Conductance and Resistance

The power of an electrolyte to conduct electric current is called conductance or conductivity.

The conductance and resistance have reciprocal relationship such as:

$$C \propto \frac{1}{R}$$

Therefore, the unit of conductance is ohm^{-1} or mho and is denoted by Ω^{-1}. Its SI unit is Siemen (S).

The resistance of a conductor is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) of that conductor such as

$$R \propto l \qquad \text{and} \qquad R \propto \frac{1}{a}$$

i.e. $$R \propto \frac{l}{a} \qquad \text{or} \qquad R = \rho \cdot \frac{l}{a}$$

where, ρ is again a proportionality constant, called specific resistance or resistivity.

If $l = 1$ cm and $a = 1\ \text{cm}^2$, then $R = \rho$.

Thus, specific resistance is said to be the resistance of a conductor of 1 cm length and having a cross-sectional area of $1\ \text{cm}^2$. The unit of specific resistance is ohm-cm. The factor, $\frac{l}{a}$ is known cell constant and is expressed in cm^{-1}.

Specific Conductance

The reciprocal of specific resistance is known as specific conductance, i.e. the conductance of a solution of 1 cm length and having area of cross-section $1\ \text{cm}^2$. It is represented by κ (kappa).

$$\kappa = \frac{1}{R} \times \frac{l}{a} \quad \text{or} \quad \kappa = C \times \frac{l}{a}$$

Here, C and R are conductance and resistance respectively.

Units of specific conductance are $\text{ohm}^{-1}\ \text{cm}^{-1}$ or mho cm^{-1} or siemens m^{-1} (in SI system).

Equivalent Conductance

The conducting power of all the ions produced by dissolving 1g equivalent of an electrolyte in a given solution is known as its equivalent conductance . It is represented by λ_{eq} or Λ. Equivalent conductance and specific conductance can be related as,

$$\lambda_{\text{eq}} \text{ or } \Lambda = \frac{\kappa \times 1000}{C_{\text{eq}}\ (N)}$$

where, C_{eq} = concentration of solution in equivalent per litre (i.e. normality). Its units are $\text{ohm}^{-1}\text{cm}^2\ (\text{equiv}^{-1})$ or $\text{mho cm}^2\ (\text{equiv}^{-1})$ or $\text{S cm}^2\ (\text{g - equiv}^{-1})$.

Molar Conductance

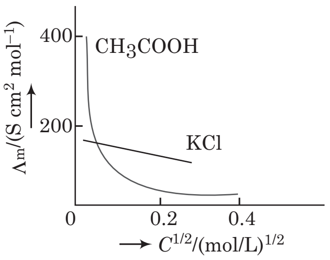
The conducting power of all the ions produced by dissolving 1 g mole of an electrolyte in solution is known as molar conductance of that solution. It is represented by λ_m or μ. Molar conductance and specific conductance can be related as

$$\lambda_{\text{eq}} \text{ or } \mu = \frac{\kappa \times 1000}{M}$$

where, M = concentration in mol/ L, i.e. molarity of the solution. Its units are $\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ or $\text{mho cm}^2\ \text{mol}^{-1}$ or $\text{S cm}^2\ \text{mol}^{-1}$.

Limiting Molar Conductivity

When the concentration approaches zero, the molar conductance reaches a limiting value, known as limiting molar conductivity and is denoted as Λ°_{m}. The variation in Λ_m with concentration is different for strong and weak electrolytes as shown in the figure below.



Molar conductance *vs* $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

For Strong Electrolytes

For strong electrolytes, Λ_m increases slowly with dilution. This can be represented by equation, Debye-Huckel-Onsager equation.

$$\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$$

If we plot Λ_m against $\sqrt{C}$, we get a straight line with slope as $-A$ and intercept as Λ°_m. The value of A depends on the type of electrolyte. Thus, $NaCl, CaCl_2, MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolytes, respectively. All electrolytes of a particular type have the same value of A.

For Weak Electrolytes

With dilution, the degree of dissociation increases for weak electrolytes as it results in increase in the number of ions. In case of weak electrolytes, the Λ°_m value increases steeply with dilution, especially in the low concentration region. In this region, the graph of weak electrolytes in a plot of Λ_m against $\sqrt{C}$ becomes parallel to the Y-axis. So, the limiting molar conductivity of a weak electrolyte cannot be determined by extrapolation of the plot. It is rather determined by applying the Kohlrausch law of independent migration of ions.

Kohlrausch's Law

Kohlrausch examined Λ°_m values for a number of strong electrolytes and found that for a pair of electrolytes with the same negative ion but differing only in the positive ion, the difference between the Λ°_m values is constant.

e.g.
$$\begin{aligned}\Lambda^\circ_{m\,(KCl)} - \Lambda^\circ_{m\,(NaCl)} &= \Lambda^\circ_{m\,(KBr)} - \Lambda^\circ_{m\,(NaBr)}\\ &= \Lambda^\circ_{m\,(KI)} - \Lambda^\circ_{m\,(NaI)}\\ &= 23.4\ \Omega^{-1}cm^2mol^{-1}\\ &\quad \text{or } (S\,cm^2mol^{-1})\end{aligned}$$

Similarly, with a common cation, the difference between Λ°_m values is also found to be constant.

$$\begin{aligned}\Lambda^\circ_{m\,(KBr)} - \Lambda^\circ_{m\,(KCl)} &= \Lambda^\circ_{m\,(NaBr)} - \Lambda^\circ_{m\,(NaCl)}\\ &= 1.8\ \Omega^{-1}cm^2mol^{-1}\\ &\quad \text{or } (S\,cm^2mol^{-1})\end{aligned}$$

The above observation led to formulate the Kohlrausch law of independent migration of ions.

It states that limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and the anion of the electrolyte.

e.g. $$\Lambda^\circ_{m\,(NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

where, $\Lambda^\circ_{m\,(NaCl)}$ is the limiting molar conductivity of NaCl and $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivities of sodium and chloride ions.

In general, if an electrolyte produces ν_+ cations and ν_- anions, then the above equation becomes,

$$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$$

Applications of Kohlrausch's Law

The applications of Kohlrausch's law are given below:

(i) The molar conductivity of weak electrolytes at infinite dilution can be calculated using Kohlrausch's law.

(ii) Degree of dissociation of weak electrolyte (like acetic acid) at a given concentration can be calculated.

(iii) Knowing the degree of dissociation α, the dissociation constant (K) of the weak electrolyte, at a given concentration of the solution, can be calculated.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 Which of the following solutions of KCl will have highest specific conductance? **[2019]**

(a) 0.0001 N (b) 0.001 N
(c) 0.01 N (d) 1.0 N

Sol (*d*) Conductance of one cm^3 of an electrolyte in solution is called specific conductance (κ). For strong electrolyte (e.g. KCl). The equivalent conductance is given as,

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

(where, Λ_e = equivalent conductance, N = normality)

Or, specific conductance (κ) $\propto$ normality (N)

$\therefore$ Higher the normality of solution higher will be its specific conductance. Thus, 1 N solution of KCl will have highest specific conductance.

Q.2 Write the unit of cell constant. **[2016]**

Sol Unit of cell constant is cm^{-1}.

Q.3 What is the relationship between chemical equivalent and electrochemical equivalent of an element ? **[2014, 2012, 2007, Textbook]**

Sol The relationship between chemical equivalent and electrochemical equivalent of an element is as follows:

$$\text{Electrochemical equivalent} = \frac{\text{Chemical equivalent}}{96500}$$

Q.4 What is obtained at cathode during electrolysis of aqueous NaCl solution? **[2012 Instant]**

Sol At cathode, the electrolysis of aq. NaCl solution leads to the liberation of hydrogen gas as shown below: $H_2O(l) + e^- \longrightarrow \frac{1}{2} H_2(g) + OH^-(aq)$

Q.5 $\Omega^{-1}\ cm^{-1}$ is the unit of **[2012 Instant]**

(a) specific conductance (b) equivalent conductance
(c) cell constant (d) molar conductance

Sol (*a*) $ohm^{-1}cm^{-1}$ or mho cm^{-1} is the unit of specific conductance.

Q.6 Find the number of coulombs required for the conversion of one mole of MnO_4^- to one mole of Mn^{2+}. **[2011]**

(a) 96500 (b) 95600 × 3
(c) 96500 × 5 (d) 96599 × 7

Sol (*c*) $\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$

Change in oxidation number = 5

The number of Coulombs required for the conversion of one mole of MnO_4^- to Mn^{2+} = 5 × 96500 C.

Q.7 Calculate the amount of Cu deposited when a current, which can deposit 10.8 g of Ag from silver nitrate solution, is passed through $CuSO_4$ solution. **[2008]**

Sol Equivalent deposited of silver = $\frac{10.8}{108} = \frac{1}{10}$

Equivalent mass of copper = $\frac{63.5}{2}$ = 31.75 g eq.

Hence, amount of Cu deposited by $\frac{1}{10}$ equivalent of silver = $\frac{31.75}{10} = 3.175$ g

Q.8 What is the unit of molar conductance? **[2008, Textbook]**

Sol $\Omega^{-1}\ m^2\ mol^{-1}$ is the unit of molar conductance.

Q.9 What is the charge on one mole of electrons? **[2006]**

Sol Charge on one mole of electrons

$$= 1.6021 \times 10^{-19} \times 6.022 \times 10^{23}$$

($\because$ charge on 1 electron = 1.6021×10^{-19} Coulombs)

$\simeq$ 96500 Coulombs = 1 Faraday

Q.10 Write two applications of electrolysis. **[2006]**

Sol The two applications of electrolysis are,

(i) for electroplating
(ii) for refining of metals **(2 × ½ = 1)**

Q.11 What is the unit of equivalent conductance? **[2006, 2000, Textbook]**

Sol $\Omega^{-1}m^2\ (g\text{-}eq)^{-1}$ is the unit of equivalent conductance.

Q.12 What do you mean by strong and weak electrolytes? **[2003]**

Sol The electrolytes which dissociate completely into ions are called strong electrolytes. e.g. NaCl, NaOH etc.

The electrolytes which do not ionise completely in aqueous as well as in molten state are called weak electrolytes. e.g. H_2CO_3, CH_3COOH etc.

Q.13 How does equivalent conductance vary with dilution? **[2002]**

Sol Equivalent conductance increases with increase in dilution as the number of ions increases with dilution.

Q.14 How many Coulombs of electricity are required to produce 20 g of calcium from molten $CaCl_2$? **[2001, Textbook]**

Sol $CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$

2 Faraday (2 × 96500 Coulombs) of electricity are required to produce 20 g of calcium from molten $CaCl_2$.

Q.15 One Faraday of electricity will deposit ……… weight of a metal. **[2001, Textbook]**

Sol 1 g-equivalent.

Q.16 A current of 0.5 A flowing for 30 min deposits 0.2964 g of a metal at the cathode. Calculate the equivalent mass of the metal. **[2001]**

Sol Given that, current = 0.5 A, time = 30 min = 1800s

Quantity of electricity = current × time

$= 0.5 \times 1800 = 900$ Coulombs

900 Coulombs of electricity deposits 0.2965 g of a metal.

∴ Amount of metal deposited by 96500 Coulombs of electricity $= \dfrac{0.2965 \times 96500}{900} = 31.79$ g

Q.17 Define specific conductance. **[2000, Textbook]**

Sol The reciprocal of specific resistance is known as specific conductance i.e. the conductance of a solution of 1 cm length and having area of cross-section equal to 1 cm^2.

Important Questions

Q.18 The electric charge required for electrolytic deposition of one gram equivalent of a substance is **[Textbook]**

(a) one ampere for one second
(b) 96500 Coulombs
(c) charge on one mole of electrons
(d) one ampere for one hour

Sol (*b*) The amount of electric charge required to pass through the electrolyte to liberate or deposit one gram equivalent of the substance is called Faraday's constant (F).

1 Faraday $= 96500$ C mol^{-1}

Q.19 Faraday's law of electrolysis are related to **[Textbook]**

(a) the atomic number of cation
(b) the atomic number of anion
(c) equivalent mass of electrolyte
(d) speed of the cation

Sol (*c*) Faraday's law of electrolysis are related to equivalent mass of the electrolyte.

Q.20 Molten sodium chloride conducts electricity due to the presence of ……… . **[Textbook]**

(a) free electrons (b) free ions
(c) free molecules
(d) atoms of sodium and chlorine

Sol (*b*) Molten sodium chloride conducts electricity due to the presence of free ions. In order to conduct electricity, a substance must have charged particles, such as ions, that are free to move through it.

Q.21 The unit of specific conductance is ……… **[Textbook]**

(a) Ohm (b) $Ohm^{-1}cm^{-1}$
(c) Coulomb (d) Faraday

Sol (*b*) The unit of specific conductance is ohm^{-1} cm^{-1}.

Q.22 The charge (in Coulomb) on the Na^+ ion (oxide) is ……… **[Textbook]**

(a) 96500 (b) $4.8 \times 10^{+19}$
(c) 4.8×10^{-19} (d) 1.6×10^{-19}

Sol (*d*) Sodium ion (Na^+) has 11 protons and 10 electrons, therefore its net charge is one unit electronic charge, i.e. 1.6×10^{-19} C.

Q.23 96500 Coulomb will deposit ……… of metal. **[Textbook]**

(a) one electrochemical equivalent
(b) one g
(c) one g equivalent
(d) one g molecular mass

Sol (*c*) 96500 Coulomb of electric charge will deposit one gram equivalent of any substance.

$$F = \frac{W_A}{W_B} = \frac{\text{Equivalent mass of } A}{\text{Equivalent mass of } B}$$

Q.24 Which one of the following is a weak electrolyte? **[Textbook]**

(a) Sodium chloride (b) Copper sulphate
(c) Acetic acid (d) Sodium chloride

Sol (*c*) Acetic acid (CH_3COOH) is an example of a weak electrolyte. Its strength is determined by its acid dissociation constant, pK_a value.

Q.25 ……… is an example of strong electrolyte. **[Textbook]**

(a) Ammonium hydroxide (b) Acetic acid
(c) Sodium acetate (d) Sodium chloride

Sol (*d*) Sodium chloride (NaCl) is a strong electrolyte because it is a salt that dissociates completely in water.

Q.26 ……… grams of chlorine can be prepared by the electrolysis of molten sodium chloride with 10 A current passed for 10 min. **[Textbook]**

(a) 2.2 (b) 4.4 (c) 3.8 (d) 5

Sol (*a*) Given, Current $(i) = 10A$

Time $(t) = 10$ min $= 60 \times 10 = 600$ s.

Quantity of electricity $= i.t = 10 \times 600 = 6000$ C

$\because$ 96500 Coulombs produces 35.5 g of chlorine.

$$\therefore \text{ 6000 Coulombs produce} = \frac{35.5}{96500} \times 6000$$
$$= 2.2 \text{ grams of chlorine}$$

Q.27 Conductance of a solution ……… with dilution. **[Textbook]**

Sol increases

Q.28 Amount of substance liberated by the passage of one Coulomb of electricity through an electrolyte is called ……… . **[Textbook]**

Sol electrochemical equivalent or Faraday's constant

Q.29 Conduction of electricity in solution is due to ……… . **[Textbook]**

Sol ions

Q.30 Equivalent conductance of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 Ω^{-1} cm^{-2} respectively. The equivalent conductance of CH_3COOH is

(a) 268.18 Ω^{-1} / cm^{-2} (b) 390.71 Ω^{-1} / cm^{-2}

(c) 398.28 Ω cm^2 (d) 540.87 Ω cm^2

Sol (*b*) From Kohlrausch's law

$$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + [\Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}]$$
$$= 91 + 426.16 - 126.45$$
$$= 390.71 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

Q.31 The quantity of electricity needed to liberate 0.5 g equivalent of an element, during electrolysis is

(a) 48250 Coulombs (b) 48250 Faraday

(c) 19300 Coulombs (d) 19300 Faraday

Sol (*a*) Electricity needed to liberate

$$0.5 \text{ g equivalent} = \frac{1}{2} \text{ Faraday} = \frac{1}{2} \times 96500 \text{ C}$$
$$= 48250 \text{ Coulombs}$$

Q.32 Ions (cations or anions) do not contribute a fixed conductance at infinite dilution.
(Correct the sentence)

Sol Ions (cations or anions) contribute a fixed conductance at infinite dilution.

Q.33 Suggest a way to determine the Λ°_m value of water.

Sol The molar conductance of water at infinite dilution can be obtained from the knowledge of molar conductances at infinite dilution of sodium hydroxide, hydrochloric acid and sodium chloride (all strong electrolytes). This is in accordance with Kohlrausch's law.

$$\Lambda^\circ_{m(H_2O)} = \Lambda^\circ_{m(NaOH)} + \Lambda^\circ_{m(HCl)} - \Lambda^\circ_{m(NaCl)}$$

Q.34 What is the unit of cell constant?

Sol cm^{-1} is the unit of cell constant.

2 MARK *Questions*

Exams' Questions

Q.35 Equivalent conductance at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.45 mho cm^2 g equivalent^{-1} respectively. Calculate the equivalent conductance of NH_4OH at infinite dilution. **[2016]**

Sol From Kohlrausch law,

$$\lambda^\circ_{m_{NH_4OH}} = \lambda^\circ_{m_{NH_4Cl}} + [\lambda^\circ_{m_{NaOH}} - \pi^\circ_{NaCl}]$$
$$= 129.8 + (217.4 - 108.45)$$
$$= 238.75 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

(2)

Q.36 State Kohlrausch's law. Discuss with an example. **[2012, 2005, 2003, 2001]**

Sol Kohlrausch's law states that limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and the anion of the electrolyte, e.g. $\Lambda^\circ_m(NaCl) = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$

where, $\Lambda^\circ_m(NaCl)$ is the molar conductivity of NaCl and $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivities of sodium and chloride ions. **(2)**

Q.37 Give two applications of Kohlrausch's law. **[2011]**

Sol The two applications of Kohlrausch's law are,

(i) the molar conductivity of weak electrolytes at infinite dilution can be calculated using Kohlrausch's law. **(1)**

(ii) degree of dissociation of weak electrolyte (like acetic acid) at a given concentration can be calculated. **(1)**

Q.38 Match Column I with Column II.

	Column I		Column II
(a)	One Faraday	(i)	6.24×10^{18} electrons
(b)	Chemical equivalent mass	(ii)	96500 Coulombs
(c)	One Coulomb	(iii)	ECE (*Z*) × 96500
(d)	Anode	(iv)	Reduction
		(v)	Oxidation

[2008]

Sol (a) → (ii), (b) → (iii), (c) → (i), (d) → (v)

One Faraday	96500 Coulombs
Chemical equivalent mass	ECE (*Z*) × 96500
One Coulomb	6.24×10^{18} electrons
Anode	Oxidation

(4 × ½ = 2)

Q.39 Define the molar conductance. **[2006]**

Sol The conducting power of all the ions produced by dissolving 1 g mole of an electrolyte in solution is known as molar conductance of that solution. It is represented by λ_m or μ.

Its units are Ω^{-1} cm^2 mol^{-1} or mho cm^2 mol^{-1} or S cm^2 mol^{-1}. **(2)**

Q.40 Why sodium cannot be extracted by electrolysis of aqueous solution of sodium chloride? **[2006, Textbook]**

Sol Sodium is a very reactive metal. On electrolysis, aqueous solution of sodium chloride produces sodium at the cathode which reacts with water to form dihydrogen gas and NaOH in solution. **(2)**

Important Questions

Q.41 The molar conductance of a solution of $AlCl_3$ is found to be 130 mho $cm^2\ mol^{-1}$ at 298 K. What would be its equivalent conductance at the same temperature? **[Textbook]**

Sol $\because$ Al forms Al^{3+} ions

$\therefore$ 1 mole of Al is equivalent to 3F of charge.

Hence, equivalent conductance of Al

$= 3 \times$ molar conductance $= 3 \times 130$

$= 390$ mho cm^2g-equiv^{-1} **(2)**

Q.42 Calculate the time required for a current of 2 A. to decompose one gram mole of water. **[Textbook]**

Sol Mass of $H_2O = 1$ g mol $= 18$ g

Equivalent mass (E) of $H_2O = \frac{18}{2} = 9$ g

$$m = Zit = \frac{E}{96500} \times i \cdot t$$

or $t = \frac{96500 \times m}{E \cdot i} = \frac{96500 \times 18}{9 \times 2 \times 60 \times 60}$ h = 26.80 h **(2)**

Q.43 A current strength of 965 A. can deposit 0.9 g of Al metal in 20 sec. What is the efficiency of electrolysis? **[Textbook]**

Sol Molar mass of Al = 26.98 g mol^{-1}

Equivalent mass of Al $= \frac{26.98}{3} = 8.99 \approx 9$ g eq

In 20 s, expected amount of Al

$\Rightarrow m = \frac{E}{96500} \times i \times t \Rightarrow m = \frac{9 \times 965}{96500} \times 20 = 1.8$ g

Actual amount of Al deposited = 0.9 g

Efficiency $= \frac{0.9}{1.8} \times 100 = 50\%$ **(2)**

Q.44 The conductivity of a 0.20 M KCl solution at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

Sol Given, the conductivity is $\kappa = 0.0248$ S cm^{-1} and the concentration is $C = 0.20$ M.

Then molar conductivity is calculated as,

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$ **(1)**

= (0.0248 × 1000)/ 0.20

= 124 S $cm^2\ mol^{-1}$ **(1)**

Q.45 The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?

Sol Given, Conductivity, $\kappa = 0.146 \times 10^{-3}$ S cm^{-1}

Resistance, $R = 1500\ \Omega$

$\therefore$ Cell constant $= \kappa \times R$ **(1)**

$= 0.146 \times 10^{-3} \times 1500 = 0.219\ cm^{-1}$ **(1)**

3 MARK *Questions*

Important Questions

Q.46 An electronic current is passed through two solutions (A) $AgNO_3$ and (B) a solution of 10 g of blue vitriol in 500 mL of water using platinum electrodes separately. After 30 min, it was found that 1.307 g Ag was deposited. What is the concentration of Cu^{2+} after electrolysis? **[Textbook]**

Sol Amount of current required to deposit 1.307 g of Ag is:

from formula, $W = Zit$

$$1.307 = \frac{107.8 \times i \times 30 \times 60}{96500}$$

$\therefore$ $i = 0.649$ A **(1)**

Now, same amount of current is required for deposition of copper.

$\therefore$ Amount of Cu deposited

$\therefore$ $W = Zit$

$= \frac{63.5}{2} \times \frac{30 \times 60 \times 0.649}{96500}$

$= 0.384$ g **(1)**

The concentration of blue vitriol solution is given by

$$M = \frac{\text{Number of moles}}{\text{Volume of solution in L}} = \frac{\frac{10\text{ g}}{159.6\text{ g mol}^{-1}}}{500 \times 10^{-3}\text{ L}} = 0.125\text{ M}$$

Concentration of $CuSO_4$ that gets deposited is,

$$= \frac{\frac{0.384\text{ g}}{159.6\text{ g mol}^{-1}}}{500 \times 10^{-3}\text{ L}} = 4.8 \times 10^{-3}\text{ M}$$

$\therefore$ Concentration of Cu^{2+} after electrolysis

$= 0.125\text{ M} - 4.8 \times 10^{-3}\text{ M} = 0.120$ M **(1)**

Q.47 Which of the following solutions has larger molar conductance?

(i) 0.10 M solution which has resistivity equal to 58 Ω cm.

(ii) 0.08 M solution having conductivity equal to $2.0 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Sol (i) $\Lambda_m = \frac{1}{\rho} . \frac{1000}{C} = \frac{1}{58\ \Omega\ cm} \times \frac{1000\ cm^3\ L^{-1}}{0.1\ mol\ L^2}$ **(1)**

$= 172.4\ \Omega^{-1}\ cm^2\ mol^{-1}$ **(1)**

$$\text{(ii)}\ \Lambda_m = \kappa\frac{1000}{C} = \frac{2\times10^{-2}\ \Omega\ \text{cm}^{-1}\times1000\ \text{cm}^3\ \text{L}^{-1}}{0.08\ \text{mol L}^{-1}}$$
$$= 250\ \Omega^{-1}\text{cm}^2\ \text{mol}^{-1}$$

Thus, solution (ii) has larger molar conductance. **(1)**

Q.47 The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given, $\lambda^\circ(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^\circ(HCOO^-) = 54.6$ S cm^2 mol^{-1}

Sol ***Step*** I Calculation of degree of dissociation (α) of HCOOH, $\Lambda_m = 46.1\ \text{S cm}^2\text{mol}^{-1}$

$$\Lambda^\circ_{m(HCOOH)} = \lambda^\circ_{m(HCOO^-)} + \lambda^\circ_{m(H^+)}$$
$$= (54.6 + 349.6)\ \text{S cm}^2\text{mol}^{-1}$$
$$= 404.2\ \text{S cm}^2\ \text{mol}^{-1}$$
$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{(46.1)\ \text{S cm}^2\text{mol}^{-1}}{(404.2)\ \text{S cm}^2\text{mol}^{-1}} = 0.1140 \quad \textbf{(1)}$$

Step II Calculation of dissociation constant

$$\text{HCOOH}(aq) \xrightleftharpoons{\text{Water}} \text{HCOO}^-\ (aq) + \text{H}^+\ (aq)$$

Initial	C	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Dissociation constant,

$$K_a = \frac{[\text{HCOO}^-]\ [\text{H}^+]}{[\text{HCOOH}]} = \frac{C\alpha\times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \quad \textbf{(1)}$$

Substituting values,

$$K_a = \frac{(0.025\ \text{mol L}^{-1})\times(0.114)^2}{(1-0.114)} = \frac{(3.249\times10^{-4}\ \text{mol L}^{-1})}{(0.886)}$$
$$= 3.67\times10^{-4}\ \text{mol L}^{-1}$$
$$\therefore\ \alpha = 0.114 \quad \text{and} \quad K_a = 3.67\times10^{-4}\ \text{mol L}^{-1} \quad \textbf{(1)}$$

7 MARK *Questions*

Exams' Questions

Q.49 State and explain Kohlrausch's law of independent migration of ions. **[2018]**

The equivalent conductance of infinite dilution (Λ_0) for sodium acetate, sodium chloride and hydrochloric acid are 78, 109 and 384 $ohm^{-1}cm^2$ g eq^{-1} respectively. Calculate the Λ_0 of acetic acid.

Sol Kohlrausch's law of independent migration of ions states that "at infinite dilution, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the other ion with which it is associated. The value of equivalent conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions".

So, $\Lambda_0 = \lambda^\circ_a + \lambda^\circ_c$

Kohlrausch examined Λ_0 values for a number of strong electrolytes and found that for a pair of electrolytes with the same negative ion but differing only in the positive ion, the difference between the Λ_0 values is constant.

e.g. $\Lambda_{0(KCl)} - \Lambda_{0(NaCl)} = \Lambda_{0(KBr)} - \Lambda_{0(NaBr)}$
$= \Lambda_{0(KI)} - \Lambda_{0(NaI)} = 23.4\ \Omega^{-1}\text{cm}^2\text{g eq}^{-1}\ (\text{S cm}^2\text{g eq}^{-1})$

Similarly, with a common cation, the difference between Λ_0 values is also found to be constant.

$$\Lambda_{0(KBr)} - \Lambda_{0(KCl)} = \Lambda_{0(NaBr)} - \Lambda_{0(NaCl)}$$
$$= 1.8\ \Omega^{-1}\text{cm}^2\ \text{g eq}^{-1}(\text{S cm}^2\text{g eq}^{-1})$$

According to Kohlrausch's law,

$$\Lambda_0(CH_3COOH) = \Lambda_0(H^+) + \Lambda_0(CH_3COO^-)$$
$$= \Lambda_{0(H^+)} + \Lambda_{0(Cl^-)} + \Lambda_{0(CH_3COO^-)} + \Lambda_{0(Na^+)} - \Lambda_{0(Cl^-)} - \Lambda_{0(Na^+)}$$
$$= \Lambda_{0(HCl)} + \Lambda_{0(CH_3CO\overset{-}{O}\overset{+}{N}a)} - \Lambda_{0(NaCl)}$$
$$= (384 + 78 - 109)\ \text{ohm}^{-1}\ \text{cm}^2\ \text{g eq}^{-1}$$
$$= 353\ \text{ohm}^{-1}\ \text{cm}^2\text{g eq}^{-1}$$

(7)

Q.50 Define specific, equivalent and molar conductance. Write their units. Derive the relation between specific conductance and molar conductance. What is the effect of dilution on specific and equivalent conductance ? **[2016]**

Sol **Specific conductance** The reciprocal of specific resistance is known as specific conductance, i.e. the conductance of a solution of 1 cm length and having 1 cm^2 area of cross-section. It is represented by κ (kappa).

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

Here, C and R are conductance and resistance respectively.

Units of specific conductance are Ω^{-1} cm^{-1} or mho cm^{-1} or Siemens m^{-1} (in SI system).

Equivalent conductivity The conducting power of all the ions produced by dissolving 1g equivalent of an electrolyte in a given solution is known as its equivalent conductivity. It is represented by λ_{eq}. Its units are Ω^{-1} cm^2 ($equiv^{-1}$) or mho cm^2 ($equiv^{-1}$) or S cm^2 (g-$equiv^{-1}$).

Molar conductivity The conducting power of all the ions produced by dissolving 1 g mole of an electrolyte in solution is known as molar conductivity of that solution. It is represented by λ_m or μ. Molar conductance and specific conductance can be related as λ_m or $\mu = \frac{\kappa\times1000}{M}$

where, M = concentration in mol/L, i.e. molarity of the solution. Its units are Ω^{-1} cm^2 mol^{-1} or mho cm^2 mol^{-1} or S cm^2 mol^{-1}.

Effect of dilution on specific and equivalent conductance Conductivity always decreases with decrease in concentration (i.e. with dilution) for both strong and weak electrolytes. This is due to the fact that the number of ions that carry current in a unit volume of solution always decreases with decrease in concentration. **(7)**

Q.51 State and explain Faraday's laws of electrolysis. When a current of 24 A strength is passed through $AgNO_3$ solution for 10 min, 16 g of silver is deposited. Find out the electrochemical equivalent of silver. **[2012]**

Sol **Faraday's law of electrolysis** Refer to the text on page 46. **(4)**

Problem $W = 16\,\text{g}, I = 24\ \text{A}, t = 10 \times 60\ \text{s}$

Now, $Z = \dfrac{W}{It} = \dfrac{16}{24 \times 600} = 0.0011\,\text{g/C}$ **(3)**

Q.52 (i) Define specific and equivalent conductance. How are they related ?

(ii) 0.05 M NaOH solution offered a resistance of 31.6 Ω in a conductivity cell at 298 K. If the cell constant of the cell is $0.376\ \text{cm}^{-1}$, calculate molar conductance of NaOH solution. **[2011]**

Sol (i) Refer to the text on page 74. **(4)**

(ii) Given that,

Molarity of NaOH solution = 0.05 M

Resistance = 31.6 Ω

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{31.6} = 0.03164\ \Omega^{-1}$$

From the equation,

Specific conductance (κ)

$$= \text{Conductance} \times \text{Cell constant}$$

$$= 0.03164\ \Omega^{-1} \times 0.376\ \text{cm}^{-1}$$

$$= 0.011896\ \Omega^{-1}\text{cm}^{-1}$$

As we know that

$$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}} = \frac{1000 \times 0.011896}{0.05} = 237.92\Omega^{-1}\text{mol}^{-1}$$ **(3)**

Q.53 State and explain Faraday's law of electrolysis. When a current of 1.5 amperes strength is passed through a solution of a salt of a metal (atomic mass =112) for 15 min, 0.783 g of the metal is deposited. Find out the valency of the metal. **[2010]**

Sol **Faraday's law of electrolysis** Refer to the text on page 46. **(4)**

Given that, Current (i) = 1.5 A

Time (t) = 15 min = 15×60 = 900 s

Atomic mass of the metal = 112 u

Amount of electricity passed = $i \times t = 1.5 \times 900$

= 1350 Coulombs

∵ 1350 Coulombs of electricity deposit 0.783 g of metal

∴ 96500 Coulombs of electricity deposit

$$= \frac{0.783}{1350} \times 96500 = 55.97\ \text{g}$$

$$\text{Valency} = \frac{\text{Atomic mass}}{\text{Equivalent mass}} = \frac{112}{55.97} = 2.001 = 2$$ **(3)**

Q.54 (i) Define equivalent conductance and specific conductance.

(ii) Discuss the effect of dilution on these conductances of an electrolyte.

(iii) The specific conductance of a decinormal solution of NaCl equals to $0.0092\ \Omega^{-1}\text{cm}^{-1}$. If ionic conductance of Na^+ and Cl^- ions are 43.0 and $65.0\,\Omega^{-1}\text{cm}^2\,(\text{g-eq})^{-1}$ respectively. Calculate the degree of dissociation of NaCl solution. **[2009]**

Sol (i) Refer to the text on page 46. **(2)**

(ii) Refer to the text on page 46. **(2)**

(iii) Given,

Specific conductance = $0.0092\ \Omega^{-1}\text{cm}^{-1}$

Ionic conductance of $Na^+ = 43.0\ \Omega^{-1}\text{cm}^{-1}$

Ionic conductance of $Cl^- = 65.0\ \Omega^{-1}\text{cm}^{-1}$

Normality of NaCl = 0.1 N

$$K(\text{NaCl}) = 1\ (Na^+) + 1(Cl^-) = 43 + 65$$

$$= 108\ \Omega^{-1}\text{cm}^2\ \text{eq}^{-1}$$

Further, $$\Lambda^\circ = \kappa \times \frac{1000}{N} = \frac{0.0092 \times 1000}{0.1}$$

$$= 92\ \Omega^{-1}\text{cm}^2\ \text{eq}^{-1}$$

Therefore, degree of dissociation $(\alpha) = \dfrac{92}{108} = 0.852$ **(3)**

Q.55 State and explain Faraday's law of electrolysis. 0.2964 g of copper was deposited on passing a current of 0.5 ampere for 30 minutes through copper sulphate solution. What is the atomic mass of copper ? **[2007]**

Sol **Faraday's law of electrolysis** Refer to the text on page 46. **(4)**

Given that, Current (i) = 0.5 A

Time (t) = 30 min = 1800 s

Quantity of electricity = 0.5 × 1800 = 900 Coulombs

∵ 900 Coulombs of electricity deposits 0.2964 g of copper.

∴ 96500 Coulombs of electricity deposit

$$\frac{0.2964 \times 96500}{900} = 31.78\ \text{g}$$

∴ Equivalent mass of copper = 31.78

Valency = 2

∴ Atomic mass of copper = 31.78×2 = 63.56 g **(3)**

Q.56 (i) Define specific and equivalent conductance. How are they related? What is the effect of dilution on them?

(ii) The specific conductivity of an $N/20$ solution of KCl at 25°C is 0.002765 mhos cm^{-1}. If the resistance of the same solution placed in the cell is 2000 Ω, what is its cell constant?

[2003, Textbook]

Sol (i) Refer to the text on page 46. **(4)**

(ii) Given that,

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

Resistance = 2000 Ω

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{2000} = 0.0005\ \Omega^{-1}$$

As we know that,

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Conductance}} = \frac{0.002765}{0.0005}$$

$$= 5.53\ \text{cm}^{-1}$$ **(3)**

Q.57 (i) State and explain Faraday's laws of electrolysis.

(ii) 0.2015 g of copper was deposited by a current of 0.25 A in 45 min. Find out the electrochemical equivalent of copper. **[2000, Textbook]**

Sol (i) **Faraday's law of electrolysis** Refer to the text on page 46. **(4)**

(ii) Given that, Current (i) = 0.25 A

time (t) = 45 min = 45 × 60 s

Quantity of electricity passed = $i \cdot t$

= 0.25 × 45 × 60 = 675 Coulombs

∵ 675 Coulombs of electricity deposit 0.2015 g of copper

∴ Electrochemical equivalent of copper

$$= \frac{0.2015}{675} = 0.0002985\ \text{g C}^{-1}$$ **(3)**

Important Questions

Q.58 The conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If the limiting molar conductivity of acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant ?

Sol Given, $\kappa = 7.896 \times 10^{-5}$ S cm^{-1},

$M = 0.00241$ mol L^{-1}

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$ **(1)**

$= (7.896 \times 10^{-5} \times 1000) / 0.00241$ S cm^2 mol^{-1}

$= (7.896 \times 10^{3-5}) / (2.41 \times 10^{-3})$ S cm^2 mol^{-1}

$= 78.96/2.41$ S cm^{2}mol^{-1} = 32.76 S cm^2 mol^{-1} **(2)**

Since, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$, the degree of dissociation is calculculated as, **(1)**

$\alpha = 32.76/390.5 = 0.084$ **(1)**

The dissociation constant, $K = \dfrac{C\alpha^2}{(1-\alpha)}$. However, since α is small, the expression is simply written as $K = C\alpha^2$.

Here, $C = M$ = concentration in mol L^{-1}.

Therefore,
$K = 0.00241 \times (0.084)^2 = 1.7 \times 10^{-5}$ mol L^{-1} **(2)**

Q.59 The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa$ / Sm^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $C^{½}$.

Find the value of Λ°_m .

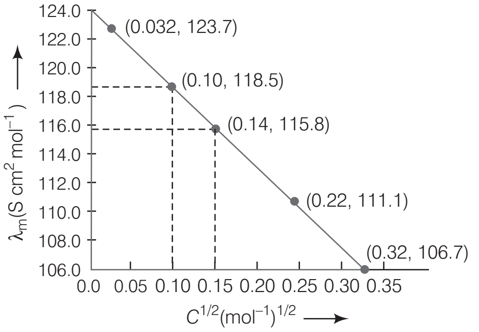
Sol According to the question, the given values are

$1\ \text{S cm}^{-1} = 100\ \text{S m}^{-1}$

or $\dfrac{1\ \text{S cm}^{-1}}{100\ \text{S m}^{-1}} = 1$ (unit conversion factor)

Conc. (M)	κ (S m^{-1})	κ (S cm^{-1})	$\Lambda_m = \dfrac{1000 \times \kappa}{\text{Molarity}}$ (S cm^2 mol^{-1})	$C^{1/2}$($M^{1/2}$)
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\dfrac{1000 \times 1.237 \times 10^{-4}}{10^{-3}}$ = 123.7	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\dfrac{1000 \times 11.85 \times 10^{-4}}{10^{-2}}$ = 118.5	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\dfrac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}}$ = 115.8	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\dfrac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}}$ ≈ 111.1	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\dfrac{1000 \times 106.74 \times 10^{-4}}{10^{-1}}$ = 106.7	0.316

(3½)



So, the graph between Λ_m and $C^{1/2}$ is shown above

Λ° = Intercept on the Λ_m axis = 124.0 S cm^2 mol^{-1} (the value of Λ_m on extrapolation to zero concentration). **(3½)**

TOPIC TEST 1

1. What is the unit of equivalent conductance in SI system? [**Ans.** $5m^2$ sq^{-1}]
2. Molten potassium chloride conducts electricity due to the presence of
   (a) free ions
   (b) free molecules
   (c) free electrons
   (d) atoms of sodium and chlorine
   [**Ans.** (a)]
3. Change on one mole of electron = ... [**Ans.** 96500 C]
4. In electrolytic cell, anode act as sink of electron (State True/False). [**Ans.** False]
5. Define specific conductance.
6. What do you mean by strong and weak electrolyte?
7. How is cell constant calculated from conductance values ?
8. What is the effect of decreasing concentration on the molar conductivity of weak electrolyte ?
9. What type of graph is obtained for Λ_m against $\sqrt{C}$?
10. The conductivity of a 0.40 M NaCl solution at 298 K is 0.0744 S cm^{-1}. Calculate its molar conductivity.
11. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 Ω . Calculate its resistivity, conductivity and molar conductivity.
12. With the help of graph, explain why is it not possible to determine Λ_m^∞ for a weak electrolyte by extrapolating the concentration *versus* molar conductance curve as for strong electrolytes.
13. Define Kohlrausch's law. How does it help in
    (i) calculation of $\Lambda°$ for a weak electrolyte?
    (ii) explaining degree of dissociation of a weak electrolyte?
14. Which one of the following solutions has larger value of molar conductance?
    (i) 0.08 M solution having conductivity equal to 2.0×10^{-2} Ω^{-1} cm^{-1}.
    (ii) 0.10 M solution having resistivity equal to 58 Ω cm.
    (iii) Why is it not possible to determine $\Lambda°$ for a weak electrolyte?
15. What amount of silver will be deposited by passing 2F electricity through two solutions containing 0.1M Ag NO_3 and 0.2 M Ag NO_3?

TOPIC ~02 Electrochemical Cells and Series, Nernst Equation, Batteries and Corrosion

Galvanic Cells

An **electrochemical cell** is a device in which chemical energy of redox reaction is converted into electrical energy. It consists of two metallic electrodes dipping in electrolytic solutions.

The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like KCN or KNO_3 or NH_4 NO_3 (inert electrolyte), etc.

This tube is called **salt bridge**. The significance of salt bridge includes:

(i) It connects the solution of two half-cells, thus completes the cell circuit.
(ii) It prevents transference or diffusion of the solutions from one half-cell to other etc.

In galvanic cell, oxidation occurs at anode and it is a negative plate. While reduction occurs at cathode and it is a positive plate.

Daniell Cell

Among the galvanic cells when cell is designed in such a manner to make the use of spontaneous reaction between Zn and Cu ion to produce an electric current, that cell is called Daniell cell.

In this cell, the following reaction occurs

$$\text{Zn }(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Cu }(s) + \text{Zn}^{2+}(aq)$$

Cell is represented as, $\text{Zn}|\text{Zn}^{2+}(C_1)||\ \text{Cu}^{2+}(C_2)\ |\text{Cu}$

The two half-cell reactions are

(i) $\text{Cu}^{2+} + 2\,e^- \longrightarrow \text{Cu}$ (reduction half reaction)
(ii) $\text{Zn}(s) \longrightarrow \text{Zn}^{2+} + 2\,e^-$(oxidation half reaction)

Standard Hydrogen Electrode

According to convention, a half-cell called standard hydrogen electrode (SHE) represented by Pt $(s)\,|\,H_2(g)$ 1atm$|\,H^+(aq)$ is assigned to zero potential at all temperatures corresponding to the reaction

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

Cell and Cell Reactions

(i) $Zn\,|\,ZnSO_4\,|\,K_2SO_4\,|\,HCl|\,H_2$, Pt

Zinc rod is dipped in zinc sulphate solution (electrolyte). Salt-bridge consists of potassium sulphate. Hydrogen gas at one atmospheric pressure is passed through platinum electrode dipped in hydrochloric acid. Zinc rod act as the anode and platinum electrode act as cathode.

At anode $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

At cathode $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

Flow of electrons takes place from zinc electrode to hydrogen electrode.

(ii) $Cu\,|Cu(NO_3)_2||\,AgNO_3|\,Ag$ with KNO_3 solution as salt-bridge.

At anode $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

At cathode $Ag^+(aq) + e^- \longrightarrow Ag\,(s)$

Copper rod dipped in $Cu(NO_3)_2$ solution acts as anode and silver rod dipped in $AgNO_3$ solution acts as cathode. Electron flows from copper to silver electrode.

(iii) $Pt, H_2|\,HCl\,|\,K_2SO_4\,|\,CuSO_4\,|\,Cu$

Platinum electrode is dipped in hydrochloric acid. Hydrogen gas under one atmospheric pressure is bubbled through it. Copper electrode is dipped in $CuSO_4$ solution. K_2SO_4 solution acts as the salt-bridge.

At anode $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

At cathode $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Electrons flow from hydrogen to copper electrode.

Electrode Potential

When a metal is placed in a solution of its ions, the metal acquires either a positive or a negative charge with respect to the solution.

On account of this, a definite potential difference is developed between the metal and the solution.

This potential difference is called electrode potential. Thus, electrode potential is the measure of the tendency of an electrode to gain or lose electrons in a half-cell.

The electrode potential can be of two types:

Oxidation Potential

The tendency of an electrode to lose electrons or to get oxidised is called its oxidation potential.

e.g.
$$M\,(s) \rightleftharpoons M^{n+}(aq) + ne^-$$
$$Zn\,(s) \rightleftharpoons Zn^{2+} + 2e^-$$

Such an electrode is negatively charged with respect to its salt solution.

Reduction Potential

The tendency of an electrode to gain electrons, i.e. to get reduced is known as reduction potential.

e.g.
$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$$

Such an electrode is positively charged with respect to its salt solution. Thus, $E_{\text{oxidation}} = -E_{\text{reduction}}$

Standard Electrode Potential

Potential difference between the metal and the metal ion in which electrode is dipped, is called electrode potential (E) in a given state.

When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as standard electrode potential (E°) of the cell. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials.

Electrode potential depends on temperature and concentration of the ion involved.

Cell Potential

The potential difference between the two half-cells is called the cell potential.

It is given by the following formula.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \text{ or } E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

Nernst Equation

It gives the relation between electrode potential, temperature and concentration of metal ions.

$$M^{n+} + ne^- \longrightarrow M$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{[M]}{[M^{n+}]}$$

When $T = 298$ K, F = 96500 C mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1} and concentration of solid M is taken as unity

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]}$$

Relationship between equilibrium constant and standard potential of the cell

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303\,RT}{nF}\log K_C$$

[where, K_C is equilibrium constant]

At equilibrium, $E_{\text{cell}} = 0$

$$E^\circ_{\text{cell}} = \frac{2.303\,RT}{nF}\log K_C = \frac{0.059}{n}\log K_C;$$

$$K_C = \text{Antilog}\left(\frac{nE^\circ_{\text{cell}}}{0.059}\right)$$

Electromotive Force of Simple Cells

EMF is the potential difference when no current is drawn from the system. It is measured in volts (V).

For standard hydrogen electrode $E^\circ_{\text{SHE}} = 0.00\,\text{V}$. SHE and calomel electrode are used as reference half-cells.

EMF of a cell is determined by connecting the voltmeter between the two electrodes of a cell. EMF depends upon the nature of electrodes and concentration of solution of the two half- cells.

e.g. Daniell cell $\text{Zn} \mid \text{ZnSO}_4\,(1\text{ M}) \| \text{CuSO}_4\,(1\text{M}) \mid \text{Cu}$ concentration of the solutions is 1 M and temperature is 298 K.

$$\text{EMF of the cell} = 1.10\text{ volts}$$

Thus, $E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$ (for oxidation potential)

and $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$ (for reduction potential)

An electrode with higher oxidation potential is called anode while an electrode with lower oxidation potential is called cathode.

Electrochemical Series

It is a series of chemical elements arranged in the increasing order of their reduction potentials.

Standard aqueous electrode potentials at 298K
(The electrochemical series)

Element	**Electrode reaction** (Reduction)	**Standard electrode reduction potential** E° (volt)
Li	$\text{Li}^+ + e^- \rightarrow \text{Li}$	– 3.05
K	$\text{K}^+ + e^- \rightarrow \text{K}$	– 2.925
Ca	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	– 2.87
Na	$\text{Na}^+ + e^- \rightarrow \text{Na}$	– 2.714
Mg	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	– 2.37
Al	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	– 1.66
Zn	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	– 0.7628
Cr	$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	– 0.74
Fe	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	– 0.44
Cd	$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	– 0.403
Ni	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	– 0.25
Sn	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	– 0.14
H_2	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+ 0.337
I_2	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+ 0.535
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+ 0.799
Hg	$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	+ 0.885
Br_2	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+ 1.08
Cl_2	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+ 1.36
Au	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+ 1.50
F_2	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+ 2.87

Electrochemical Cell and Gibbs Energy of the Reaction

To obtain maximum work from a galvanic cell, charge has to be passed reversibly.

The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, ΔG° gives the maximum work.

$\Delta G^\circ = -\,nFE^\circ_{\text{cell}}$. If E°_{cell} is positive, ΔG° = negative, cell will work.

If E°_{cell} is negative, ΔG° = positive, cell will not work.

A metal having negative reduction potential is stronger reducing agent than H_2 and a metal having positive reduction potential is weaker reducing agent than H_2.

Batteries (Commercial Cells)

A battery (which contains one or more than one electrochemical cell connected in series) or a cell that we use as a source of electrical energy is basically a galvanic cell, which converts the chemical energy of the redox reaction into electrical energy.

For a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use.

There are following types of batteries:

1. Primary Batteries

The device which provide electrical energy are called the **cell**. It can be **primary** or **secondary**.

The cell in which products cannot be changed back into reactants is called **primary cell,** e.g. Daniell cell, mercury cell, dry cell.

Dry Cell (Leclanche cell)

It consists of a zinc container which acts as anode and cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon.

The space between the electrodes is filled by a moist paste of NH_4Cl and ZnCl_2.

The reactions are

At anode $\text{Zn}(s) \longrightarrow \text{Zn}^{2+} + 2e^-$

At cathode $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

At cathode, manganese is reduced from the + 4 oxidation state to the + 3 state.

Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V, it decreases with time.

Mercury Cell

It consists of Zn - Hg amalgam as anode. The cathode is a paste of mercuric oxide (HgO) and carbon powder. The electrolyte is a paste of KOH and ZnO.

The electrode reactions are given as:

At anode

$$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

At cathode

$$HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

The overall reaction is

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The cell potential is approximately 1.35 V and remains constant during its life.

2. Secondary Batteries

A secondary cell is capable of being charged after discharging again and again,
e.g. lead storage battery, nickel-cadmium battery.

Lead Storage Battery

It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A 38% solution of sulphuric acid acts as the electrolyte.

When the battery is in use (discharging), the cell reactions are

At anode

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

The **overall reaction** is

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

During charging, the reactions are reversed.

Nickel-Cadmium cell

The overall cell reaction of Ni-Cd cell during discharging is

$$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

It is another important secondary cell.

Fuel Cells

They are galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol directly into electrical energy,
e.g. hydrogen-oxygen fuel cell, in which hydrogen and oxygen are bubbled through porous carbon electrodes into conc. KOH solution.

The electrode reactions of $H_2—O_2$ fuel cell are

At anode

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

At cathode

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

The **overall reaction** is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

$$\text{Efficiency of a cell} = \frac{\Delta G}{\Delta H} = \frac{\text{Useful work}}{\text{Total work}}$$

Corrosion

It is basically an electrochemical phenomenon in which a metal oxide or other salt of the metal forms a coating on the metal surface, e.g. rusting of iron, in which the following reactions take place:
Oxidation, at anode

$$2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e^-$$

Reduction, at cathode

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$$

The overall reaction is

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

Atmospheric oxidation (when Fe^{2+} ions are further oxidised by atmospheric oxygen).

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

Prevention of Corrosion

It can be prevented by several methods:

(i) **Barrier protection** It can be achieved by coating the metal surface with paints, oil or grease or by certain chemicals, like $FePO_4$ that provides a tough adherent film on the metal surface.

(ii) **Sacrificial protection** This method involves the protection of a metal by coating their surface by some active metal like zinc.

(iii) **Cathodic protection** This method involves the use of a more reactive (more electropositive) metal as a sacrificial anode along with the lesser reactive metal to be protected.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK *Questions*

Exams' Questions

Q.1 Cations on reaching .... gain electrons and form neutral atoms which get .... on the cathode. **[2013]**

Sol cathode, deposited

Q.2 In the electrochemical cell, oxidation takes place at …… **[2012, Textbook]**

Sol anode

Q.3 What is the standard electrode potential of hydrogen electrode? **[2011, 2005, Textbook]**

Sol Potential of standard hydrogen electrode is zero.

Q.4 Write the Nernst equation for electrode reaction.

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$ **[2010]**

Sol The Nernst equation for the given electrode reaction is

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} + \frac{0.0591}{n} \log [M^{n+}(aq)] \text{ volts}$$

Q.5 Between zinc and silver, which metal will react with dilute sulphuric acid? **[2004, 2001]**

Sol Zinc, because it lies above hydrogen in the electrochemical series.

Q.6 In an electrochemical cell, reduction takes place at …… **[2004, 2001, Textbook]**

Sol cathode

Q.7 In a cell $\text{Zn}|\text{Zn}^{2+}(aq)\ (1.0\ \text{M})||\text{Cu}^{2+}(aq)\ (1.0\ \text{M})|\text{Cu}$, the standard electrode potentials are

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu},\ E^\circ = 0.350\text{V}$$

and

$$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn},\ E^\circ = -0.7631\text{V}$$

What is the e.m.f. of the cell? **[2003]**

Sol

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$
$$= 0.35 - (-0.763) = 1.113\ \text{V}$$

Q.8 If a silver spoon is electroplated, would it be made an anode or cathode in a cell? **[2003]**

Sol It could be made the cathode in a cell as deposition of a metal takes place on the cathode.

Q.9 What is the basis on which anode or cathode is identified in a chemical cell? **[2002, Textbook]**

Sol Anode is an electrode on which oxidation takes place while cathode is an electrode on which reduction takes place.

Q.10 What is the relationship between emf of a cell and equilibrium constant? **[2002, Textbook]**

Sol The relationship between emf of a cell and equilibrium constant is as $E^\circ_{\text{cell}} = \frac{2.303RT}{nF} \log K_C$

Important Questions

Q.11 Which is the strongest reducing agent? **[Textbook]**

(a) $\text{Zn}(s)$ (b) $\text{Cr}(s)$
(c) $\text{H}_2(g)$ (d) $\text{Fe}^{2+}(aq)$

Sol (a) According to the electrochemical series the decreasing order of strength of reducing agent is as follows:

$$\text{Zn}(s) > \text{Cr} > \text{Fe}^{2+} > \text{H}_2$$

Hence, Zn is the strongest reducing agent.

Q.12 The electrode at which the electrons flow into an electrolyte is ……… **[Textbook]**

(a) anode (b) metal
(c) cathode (d) cell

Sol (*c*) When electrodes are placed in an electrolyte solution and a voltage is applied, the electrolyte will conduct electricity. Electrons cannot usually pass through the electrolyte, instead a chemical reaction occurs at the cathode that consumes electrons from the anode.

Q.13 Which of the following type of reactions occur at the anode during electrolysis? **[Textbook]**

(a) Dissociation (b) Substitution
(c) Reduction (d) Oxidation

Sol (*d*) The oxidation terminal loses electrons to the electrolyte. The negative charge moves away from the oxidation site. The positive current moves towards the oxidation site, against the flow of electrons. Since, current flows to the anode, the oxidation site is the anode of the cell.

Q.14 For a redox reaction to proceed in a cell, the e.m.f. must be **[Textbook]**

(a) positive (b) negative (c) zero (d) fixed

Sol (*a*) For a redox reaction to proceed in a cell, the e.m.f. must be positive. A redox reaction is spontaneous, if the standard electrode potential for the redox reaction, $E^\circ_{\text{redox reaction}}$ is positive.

$E^\circ_{\text{redox reaction}} = E^\circ_{\text{reduction reaction}} - E^\circ_{\text{oxidation reaction}}$

and $E^\circ_{\text{redox reaction}} > 0$

that is, $E^\circ_{\text{redox reaction}}$ is positive.

Q.15 Moles of aluminium produced by passing six Faraday of electricity is .... **[Textbook]**

(a) 2 mol (b) 6 mol (c) 3 mol (d) 1 mol

Sol (*a*) **At cathode** $Al^{3+} + \underset{3F}{3e^-} \longrightarrow Al$

3 mole of electrons are required to produce 1 mole of aluminium.

$\because$ 3F of Al = 1 mole

$\therefore$ 6F of Al $= \frac{1}{3} \times 6 = 2$ moles

Q.16 In electrochemical cell .... energy is converted to .... energy. **[Textbook]**

Sol Refer to text on page 85.

Q.17 Zinc has a .... tendency to lose electrons than copper. **[Textbook]**

Sol higher

Q.18 In a galvanic cell electron flows from .... to .... through the connecting wires. **[Textbook]**

Sol anode, cathode

Q.19 In a galvanic cell the difference between reduction potential of cathode and anode is called .... **[Textbook]**

Sol cell potential (EMF)

Q.20 An aqueous solution of silver nitrate .... be stored in a copper vessel. **[Textbook]**

Sol cannot

Q.21 The more .... the standard reduction potential, the .... is the ability to displace hydrogen from acids. **[Textbook]**

Sol negative, higher

Q.22 The standard reduction potential E° for the half- reactions are

$$Zn \longrightarrow Zn^{2+} + 2e^-, \; E^\circ = +0.76\text{ V}$$
$$Fe \longrightarrow Fe^{2+} + 2e^-, \; E^\circ = +0.44\text{ V}$$

The EMF of the cell reaction: $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is

(a) 0.32 V (b) –0.32 V
(c) 2.38 V (d) –2.38 V

Sol (*a*) From the equation,

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$= -0.44\text{V} - (-0.76\text{ V}) = +0.32\text{ V}$

Q.23 Standard electrode potentials of three metals *A*, *B* and *C* are –1.2 V, + 0.5 V and –3.0 V respectively. The reducing power of these metals will be

(a) $B > C > A$ (b) $B > A > C$
(c) $C > A > B$ (d) $A > B > C$

Sol (*c*) Reducing power increases with decrease in reduction potential.

Q.24 For a feasible cell reaction, the emf of cell must be ....

Sol For a feasible cell reaction, the emf of cell must be positive.

Q.25 In electrochemical series, the elements are arranged in the order of increasing ...... potential. **[Textbook]**

Sol reduction

2 MARK *Questions*

Exams' Questions

Q.26 $CuSO_4$ solution is electrolysed for 20 minutes with a current of 3 A. What mass of copper will be deposited at the cathode? **[2019]**

(Eq. mass of Cu = 31.75)

Sol Given, time $(t) = 20$ minutes $= 20 \times 60 = 1200$ s

Current $(i) = 3$ A

$\because Q = it = 3 \times 1200 = 3600$ C

Also,

$\because$ Eq. mass of Cu = 31.75

$\therefore$ Molar mass of Cu = 2 × 31.75 = 63.5 g

($\because$ It has (+) 2 charge)

Now,

$\because 2 \times 96500$ C charge gives Cu = 63.5 g

$\therefore$ 3600 C charge will give Cu $= \frac{63.5 \times 3600}{2 \times 96500}$

$= 1.18$ g

Thus, mass of copper (Cu) deposited at cathode = 1.18 g **(2)**

Q.27 Represent the cell and calculate the standard emf of the cell having following cell reaction :

$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

$E^\circ_{Cr^{3+}/Cr} = -0.73$ volt and

$E^\circ_{Cd^{2+}/Cd} = -0.40$ volt. **[2016, 2012, 2002]**

Sol The cell is represented as, $Cr|Cr^{3+}||Cd^{2+}|Cd$.

$E^\circ_{\text{cell}} = E^\circ_{Cd^{2+}/Cd} - E^\circ_{Cr^{3+}/Cr} = -0.40 - (-0.73) = 0.33$ V. **(2)**

Q.28 Predict whether we can store $CuSO_4$ solution in a zinc vessel from the following data. Show your calculation.

$$E^\circ_{Zn^{2+}/Zn} = -0.76\,V;$$

$$E^\circ_{Cu^{2+}/Cu} = 0.34\,V$$ **[2013, 2012, 2011]**

Sol $CuSO_4$ solution cannot be stored in zinc vessel because Zn displaces Cu from $CuSO_4$ solution giving $ZnSO_4$ and copper metal. The reaction is as follows.

$Zn + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu$

Here, Zn is anode and Cu is cathode.

Therefore, $E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}$

$= 0.34 - (-0.76) = 1.10V$

Since, E°_{cell} is positive, this reaction is feasible. **(2)**

Q.29 Calculate the standard EMF of the cell having the cell reaction.

$$Zn(s) + Co^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Co(s)$$

$E^\circ_{Zn/Zn^{2+}} = 0.76\,V$, $E^\circ_{Co/Co^{2+}} = 0.25\,V$ **[2012 Instant]**

Sol In this cell, Zn/Zn^{2+} is anode and Co/Co^{2+} is cathode. **(1)**

$\therefore E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.25 - (-0.76) = 0.51\,V$ **(1)**

Q.30 Write the Nernst equation for the electrode reaction. **[2010]**

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

Sol Nernst equation, $E = E^\circ - \dfrac{2.303RT}{nF}\log\dfrac{[M]}{[M^{n+}]}$

For solids, concentration M is taken as unity.

Hence, $E = E^\circ + \dfrac{2.303RT}{nF}\log[M^{n+}]$ **(2)**

Important Questions

Q.31 What is the difference between a galvanic cell and electrolytic cell? **[Textbook]**

Sol

	Galvanic cell	Electrolytic cell
(i)	It converts chemical energy into electrical energy.	It converts electrical energy into chemical energy.
(ii)	Anode acts as negative terminal.	Anode acts as positive terminal.
(iii)	Cathode acts as positive terminal.	Cathode acts as negative terminal.

(2)

Q.32 Given the standard electrode potentials,
$K^+/K = -2.93\,V$, $Ag^+/Ag = 0.80$
$Hg^{2+}/Hg = 0.79\,V$, $Mg^{2+}/Mg = -2.37\,V$,
$Cr^{3+}/Cr = -0.74\,V$

Arrange these metals in their increasing order of reducing power.

Sol The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials are in the order.

$K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$

Therefore, the arrangement of metals in the order of increasing reducing power will be

Ag < Hg < Cr < Mg < K **(2)**

Q.33 Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Sol When lead storage battery is recharged, electrical energy is supplied to the cell from the external source, i.e. the cell operates as an electrolytic cell during recharging. All the chemical reactions, which take place during the use of battery, are reversed at this time. **(1)**

At anode $PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$

At cathode $PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

Overall reaction $2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$ **(1)**

3 MARK *Questions*

Exams' Questions

Q.34 Write a note on hydrogen–oxygen fuel cell. **[2019]**

Sol **Hydrogen-Oxygen Fuel Cell** Fuel cells are galvanic cells, in which chemical energy from combustion of fuels is converted into electrical energy. Fuel cells are designed to convert the energy of combustion of fuels like, hydrogen, methane, methanol etc directly into electrical energy.

In hydrogen-oxygen fuel cells, hydrogen and oxygen react to form water providing electrical energy.

Overall reaction occurs as follows :

Anode $[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$

Cathode $[O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$

Overall $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

These cells have very high efficiency and are pollution-free, thus are used in space-crafts.

The H_2O produced can be used by the astronauts in space. **(3)**

Q.35 E° values for $Fe^{3+} + 3e^- \longrightarrow Fe$ and $Fe^{2+} + 2e^- \longrightarrow Fe$ are -0.036 V and -0.44 V respectively. Calculate the E° and ΔG° for the cell reaction $Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$. **[Textbook]**

Sol Given,

$Fe^{3+} + 3e^- \longrightarrow Fe \quad E^\circ = -0.036\,V \quad \ldots(1)$

$Fe^{2+} + 2e^- \longrightarrow Fe \quad E^\circ = -0.44\,V \quad \ldots(2)$

$$Fe + 2Fe^{2+} \longrightarrow 3Fe^{2+} \qquad E^\circ = 7, \Delta G^\circ = 7 \qquad \ldots(3)$$

On applying operation,

(Eq (1) × 2) – (Eq (2) × 3) = Eq (3)

$$[-6 \times F \times (-0.036)] - [-6 \times F \times (-0.44)] = -6 \times F \times E^\circ$$

$$E^\circ = 0.404 \text{ V}$$

Now, ΔG° for Eq (3) is $-6 \times F \times 0.40$ V

$$= -6 \times 96500 \text{ C} \times 0.40 \text{ V}$$

$$= 233916 \text{ J} = 233.9 \text{ kJ}$$ **(3)**

Q.36 Find the stability constant of the complex $[Zn(NH_3)_4]^{2+}$ formed in the reaction

$$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$$

Given that, $E^\circ_{Zn^{2+}/Zn} = -0.76$ V

and $E^\circ_{[Zn(NH_3)_4]^{2+}/Zn,\ 4NH_3}, = -1.03$ V

Sol Given that,

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s);\ E^\circ = -0.76 \text{ V} \qquad \ldots(i)$$

$$[Zn(NH_3)_4]^{2+} + 2e^- \rightleftharpoons Zn(s) + 4NH_3;\ E^\circ = -1.03 \text{ V}$$

or $$Zn(s) + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+} + 2e^-;$$

$$E^\circ = 1.03 \text{ V} \qquad \ldots(ii)$$

Adding Eq. (i) and (ii), we get the overall reaction.

$$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$$ and

$$E^\circ_{cell} = 1.03 - 0.76 \text{ V} = 0.27 \text{ V}$$ **(1)**

$$E^\circ_{cell} = \frac{0.0591}{n} \log K,\ n = 2$$

or $$\log K = \frac{0.27 \times 2}{0.0591} = 9.1371$$ **(1)**

or $$K = \text{antilog } 9.1371 = 1.371 \times 10^9$$ **(1)**

7 MARK *Questions*

Exams' Questions

Q.37 Describe the construction and working of Daniell cell.

The following reaction occurs in a cell

$$Zn(s) + Co^{2+}(aq) \rightleftharpoons Co(s) + Zn^{2+}(aq)$$

Write the electrode reaction and find out the emf of the cell.

Given,

$$Zn(s) \longrightarrow Zn^{2+}(aq), \quad E^\circ = 0.76 \text{ V}$$

$$Co(s) \longrightarrow Co^{2+}(aq), \quad E^\circ = 0.28 \text{ V}$$

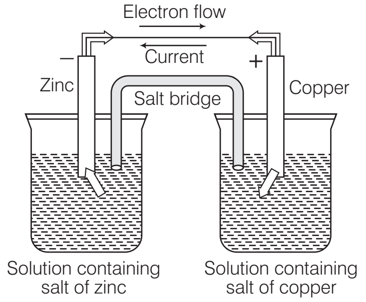
[2015, Textbook]

Sol The construction and working of a Daniell cell is as follows:

Daniell cell

It consists of zinc rod dipped in zinc sulphate solution and a copper rod dipped in copper sulphate solution. These two solutions are connected by a salt bridge as shown in figure given below. Salt bridge carries out two important functions. (i) it completes the circuit and (ii) it maintains the electrical neutrality of the solution in the half-cells. The zinc and copper rods are connected by metallic wire.

The construction of a **Daniell cell** is as shown in the figure below:



An electrical potential energy of 1.1 V is generated from the cell when the concentration of Zn^{2+} and Cu^{2+} ions is 1 mol dm^{-3}. **(3)**

If an external opposite potential is applied in the galvanic cell and increased slowly, it is found that the reaction continues to take place till the opposing voltage reaches the value 1.1V. Then, the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction.

It can be described as follows :

***Case* I** When the external potential is lower than 1.1V.

Under this condition, electrons flow from Zn rod to Cu rod. Hence, current flows from Cu to Zn, zinc dissolves at anode and copper deposits at cathode.

***Case* II** When the external potential is equal to 1.1V.

Under this condition, chemical reactions in the cell stop and there is no flow of electrons or current. **(2)**

***Case* III** When the external potential is more than 1.1V.

Under this condition, the reactions are reversed and so the polarity of the electrodes are also reversed. This cell is then called an **electrolytic cell.** Now, electrons flow from Cu to Zn and current flows from Zn to Cu. Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

At anode $Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)

At cathode $Co^{2+} + 2e^- \longrightarrow Co$ (Reduction)

Overall cell reaction is,

$$Zn + Co^{2+} \longrightarrow Co + Zn^{2+}$$

$$E^\circ = E_{cathode} - E_{anode}$$

$$= -0.28 - (-0.76) = +0.48\text{V}$$ **(2)**

Q.38 What is a galvanic cell? Explain with an example. Calculate the half-cell potential at 298 K for the reaction $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$, where $[Cu^{2+}]$ is 5.0 M and $E°$ is + 0.34 volt.

[2010, 2007, 2005, Textbook]

Sol **Galvanic cell with an example** Refer to the text on page 55. **(4)**

Given that, $E° = +\,0.34$ V

$[Cu^{2+}] = 5.0$ M

Reaction is $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

From the Nernst equation

$$E = E° - \frac{0.0591}{n}\log\frac{[Cu(s)]}{[Cu^{2+}]}$$

or $$E = 0.34 - \frac{0.0591}{2}\log\frac{1}{5}$$

or $$E = 0.34 - \frac{0.0591}{2}\log 2\times 10^{-1}$$

or $$E = 0.34 + 0.0295\ \log 2$$

or $$E = 0.34 + 0.0295 \times 0.3010 \text{ or } E = 0.35 \text{ V}$$ **(3)**

Important Questions

Q.39 Using the standard electrode potentials given in table in text, predict, if the reaction between the following is feasible.

(i) $Fe^{3+}(aq)$ and $I^-(aq)$

(ii) $Ag^+(aq)$ and Cu (*s*)

(iii) $Fe^{3+}(aq)$ and $Br^-(aq)$

(iv) Ag (*s*) and $Fe^{3+}(aq)$

(v) $Br_2(aq)$ and $Fe^{2+}(aq)$

Given standard electrode potentials

$$E^\circ_{1/2I_2,I^-} = 0.541\,\text{V},\quad E^\circ_{Cu^{2+},Cu} = 0.34\,\text{V}$$

$$E^\circ_{1/2Br_2,\,Br^-} = 1.09\ \text{V},\quad E^\circ_{Ag^+,Ag} = 0.80\,\text{V}$$

$$E^\circ_{Fe^{3+},Fe^{2+}} = 0.77\ \text{V}$$

Sol The reaction will be feasible, if e.m.f. of the cell reaction is positive.

(i) $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2$

$$E^\circ_{cell} = E^\circ_{Fe^{3+},Fe^{2+}} - E^\circ_{1/2\,I_2,\,I^-}$$

$= 0.77 - 0.54 = 0.23$ V (feasible) **(1½)**

(ii) $2Ag^+(aq) + Cu \longrightarrow 2Ag(s) + Cu^{2+}(aq)$

$$E^\circ_{cell} = E^\circ_{Ag^+,\,Ag} - E^\circ_{Cu^{2+},\,Cu}$$

$= 0.80 - 0.34 = 0.46$ V (feasible) **(1½)**

(iii) $Fe^{3+}(aq) + Br^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}Br_2$

$$E^\circ_{cell} = E^\circ_{Fe^{3+},\,Fe^{2+}} - E^\circ_{1/2\,Br_2,\,Br^-}$$

$= 0.77 - 1.09 = -\,0.32$ V (not feasible) **(1½)**

($\because E°_{cell}$ is negative)

(iv) $Ag\,(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$

$$E^\circ_{cell} = E^\circ_{Fe^{3+},\,Fe^{2+}} - E^\circ_{Ag^+,\,Ag}$$

$= 0.77 - 0.80$

$= -\,0.03$ V (not feasible) **(1½)**

(v) $\frac{1}{2}Br_2(aq) + Fe^{2+}(aq) \longrightarrow Br^- + Fe^{3+}$

$$E°_{cell} = E°_{1/2\,Br_2,\,Br^-} - E°_{Fe^{3+},\,Fe^{2+}}$$

$= 1.09 - 0.77$

$= 0.32$ V (feasible) **(1)**

Q.40 A cell is prepared by dipping a copper rod in 1 M $CuSO_4$ solution and a nickel rod in 1 M $NiSO_4$ solution. The standard reduction potentials of copper electrode and nickel electrode are 0.34 V and –0.25 V, respectively.

(i) What will be the cell reaction?

(ii) What will be the standard EMF of the cell?

(iii) Which electrode will be positive?

(iv) How will the cell be represented?

Sol (i) The reduction potential of the nickel electrode is less than that of copper electrode, so nickel electrode will be the anode and copper electrode will be the cathode. **(1)**

The anode reaction is $Ni \longrightarrow Ni^{2+} + 2e^-$

The cathode reaction is $Cu^{2+} + 2e^- \longrightarrow Cu$ **(1)**

The cell reaction is $Ni + Cu^{2+} \longrightarrow Ni^{2+} + Cu$ **(1)**

(ii) The standard emf of the cell will be

$$E° = E^\circ_{cathode} - E^\circ_{anode}$$

$= 0.34 - (-\,0.25)$ V $= 0.34 + 0.25$ V $= 0.59$ V **(2)**

(iii) The electrode where reduction takes place, that is, the copper electrode will be positive. **(1)**

(iv) The cell will be represented as

$$Ni(s)\ |\ Ni^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu\,(s)$$ **(1)**

Q.41 (i) Derive the relation among conductance, specific conductance and equivalent conductance. **[2014]**

(ii) The following reaction occurs in a electrochemical cell

$$Zn(s) + Co^{2+}(aq) \longrightarrow Co(s) + Zn^{2+}(aq)$$

Write the electrode reactions and compute the standard emf of the cell.

Given that, $Zn \longrightarrow Zn^{2+}$, $E° = 0.76$V.

$Co \rightarrow Co^{2+}$, $E° = 0.28$V.

Sol (i) Refer to the text on page 46. **(4)**

(ii) Given that,

$$E°_{(Zn/Zn^{2+})} = 0.76\ \text{V}$$

$$E°_{(Co/Co^{2+})} = 0.28\ \text{V}$$

The electrode reactions are

At anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$

From the relation,

$$E_{cell} = E°_{anode} - E°_{cathode}$$

$$= +0.76 - 0.28 = +0.48 \text{ V}$$ **(3)**

Q.42 Write notes on

(i) Kohlrausch's law (ii) galvanic cell

(iii) electrochemical series **[2000]**

Sol (i) Refer to the text on page 47. **(2)**

(ii) Refer to the text on pages 55. **(3)**

(iii) Refer the text on page 57. **(2)**

TOPIC TEST 2

1. $\Delta G°$ is related to $E°_{cell}$ as ....

[***Ans***. $\Delta G° = -nFE^{\circ}_{cell}$]

2. Cathode of electrochemical cell is electron source. (Correct the sentence)

[***Ans***. Anode of electrochemical cell is electron source.]

3. If an electrochemical cell is set up as usual but there is no flow of current. What do you conclude?

[***Ans***. Cell is at equilibrium.]

4. How can a lead storage cell be recharged?

5. Ignoring the water lost by evaporation, some water has still to be added periodically into the battery used in an invertor or car, why? Why this is not required in the maintenance of free batteries?

6. What will happen, if no salt bridge were used in an electrochemical cell like Zn-Cu cell?

7. $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow Cr^{3+} + 7H_2O; \ E° = 1.33 \text{ V}$

$I^- \longrightarrow I_2 + 6e^-; \ E° = 0.54 \text{ V}$

Find the value of equilibrium constant in the reaction given above.

8. It is safe to stir $AgNO_3$ solution with a copper spoon? Why or why not?

Given, $E^{\circ}_{Ag^+/Ag} = 0.80 \text{ V}$ and $E^{\circ}_{Cu^{2+}/Cu} = 0.34 \text{ V}$

9. Calculate equilibrium constant for the reaction,

$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$

The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples.

10. Calculate the standard cell potentials of the galvanic cells in which the following reaction takes place.

$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

$$E°_{Cr^{3+}/Cr} = -0.74\text{V}, \ E°_{Cd^{2+}/Cd} = -0.40\text{V}$$

Chapter Test

1 MARK Questions

1 The standard e.m.f. of a galvanic cell involving 2 moles of electrons in its redox reaction is 0.59 V. The equilibrium constant for the redox reaction of the cell is
(a) 10^{20} (b) 10^{5} (c) 10 (d) 10^{10}

2 The potential of the following cell is 0.34V at 25°C. Calculate the standard reduction potential of the copper half-cell.
$\text{Pt}\,|\,\text{H}_2(1\,\text{atm})\,|\,\text{H}^+(1\,\text{M})\,||\,\text{Cu}^{2+}(1\,\text{M})\,|\,\text{Cu}$
(a) – 3.4 V (b) + 3.4 V
(c) – 0.34 V (d) + 0.34 V

3 When lead storage battery discharges
(a) $PbSO_4$ is consumed (b) SO_2 is evolved
(c) H_2SO_4 is consumed (d) lead is formed

4 Galvanic cell is a device in which
(a) chemical energy is converted into electrical energy
(b) electrical energy is converted into chemical energy.
(c) Thermal energy from an octside source is used to drive the cell reaction
(d) Chemical energy is seen in the form of heat **[Textbook]**

[*Ans.* **1.** (a), **2.** (d), **3.** (c), **4.** (a)]

5 Specific conductance × ……… = Equivalent conductance. [*Ans.* Volume (in mL containing 1g-equivalent of electrolyte)]

6 Conductance of a solution ……… with increase in temperature. [*Ans.* Increases]

7 What is cell constant? **[Textbook]**

8 What is the unit of molar conductance? **[Textbook]**

2 MARK Questions

9 1 N salt solution surrounding two platinum electrodes, 2.1 cm apart and 6.3 cm^2 in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductance of the solution. [*Ans.* $6.66\,L^{-1}cm^2eq^{-1}$] **[Textbook]**

10 A solution of $MgSO_4$ is electrolysed for 20 min with a current of 1.5 A. What mass of magnesium is deposited at the cathode? [*Ans.* 0.22 g]

11 $Ag^+ + e^- \rightarrow Ag$; $E^\circ = +\,0.8$ V and $Zn^{2+} + 2e \rightarrow Zn$; $E^\circ = -\,0.76$ V **[Textbook]**

Calculate the cell potential for the reaction
$2Ag + Zn^{2+} \longrightarrow Zn + 2Ag^+\,(aq)$ [*Ans.* –1.56 V]

12 Standard oxidation potential of iron electrode is + 0.44 V. Calculate the potential of Fe, $FeSO_4$ (1 M) at 25°C. **[Textbook]** [*Ans.* 0.44 V]

13 Write down the working of mercury dry cell.

14 Write down the working of nickel-cadmium cell. **[Textbook]**

3 MARK Questions

15 A current of 1.7 A is passed through 300 mL of 0.16 M $ZnSO_4$ solution for 230 seconds with a current efficiency of 90%. Find the concentration of divalent zinc in solution. **[Textbook]** [*Ans.* 0.154 m]

16 What is meant by electrochemical series? How does it help in comparing the relative oxidising or reducing powers of different elements?

17 The standard potential of Ni^{2+}/Ni is – 0.236 V. If this electrode is coupled with a hydrogen electrode, the emf of the cell becomes zero. Calculate the pH of the acid used in electrode. **[Textbook]** [*Ans.* 3.99]

18 What happens to the pH of NaCl solution after electrolysis and why?

7 MARK Questions

19 Define and explain equivalent conductance and specific conductance. A 0.1 N solution of NaCl has a specific conductance of 0.00119 mho cm^{-1}. Find its equivalent conductance. [*Ans.* $17.9\,\Omega^{-1}cm^2eq^{-1}$]

20 Explain the following terms:
(i) Conductance
(ii) Specific conductance
(iii) Equivalent conductance
(iv) Molar conductance **[Textbook]**