ELECTRO CHEMISTRY



UNIT

Walther Hermann Nernst

Walther Hermann Nernst, was a German chemist known for his work in thermodynamics, physical chemistry, electrochemistry, and solid state physics. His formulation of the Nernst heat theorem helped to pave the way for the third law of thermodynamics, for which he won the 1920 Nobel Prize in Chemistry. He is also known for developing the Nernst equation in 1887. He also derived the Nernst equation for the electrical potential generated by unequal concentrations of an ion separated by a membrane that is permeable to the ion. His equation is widely used in cell physiology and neurobiology.



Learning Objectives

After learning this unit, the students will be able to

- Recognise the conductivity of electrolylic solution
- * Define the terms resistivity, conductivity equivalent and molar conductivity
- * Explain the variation of conductivity with concentration
- Apply Kohlrausch law to calculate the conductivity of weak electrolyte at infinite dilution.
- Describe an electrochemical cell
- * Differentiate between an electrochemical and electolylic cell
- Represent a galvanic cell using IUPAC cell notation
- Derive Nernst equation and apply it to calculate E_{cell}.
- * Define Faraday's Law of electrolysis
- Describe the construction of batteries
- * Explain corrosion as an electrochemical process.

INTRODUCTION

We have come across many materials in our life, and they can be broadly classified into conductors, semiconductors and insulators based on their electrical conductivity. You might have noticed that conducting materials such as copper, aluminium etc., are used to transport electrical energy from one place to another place, and the insulating materials such as PVC, Bakelite etc., in switches, circuit boards etc., Do you know how the electrical energy is generated? We know from first Law of thermodynamics that energy can neither be created nor be destroyed, but one form of energy can be converted into another form. It is not possible to create electrical energy but we can generate electrical energy in many ways i.e., by converting solar energy, wind energy, tidal energy etc.... one such a way is converting chemical energy into electrical energy as in the case of batteries. We cannot imagine a modern technological world without batteries. Hence it is important to know the principles behind this type of energy conversion. The branch of chemistry that deals with the study of electrical energy transport and the inter conversion of electrical and chemical energy is called electrochemistry. Electrochemical reactions are redox reactions and they involve the transfer of electron from one substance to another.

In this unit, we will learn about the electrical conduction, construction of batteries and the thermodynamic principles involved in electro chemical reactions.

9.1 Conductivity of electrolytic solution

We have already learnt that when an electrolyte such as sodium chloride, potassium chloride etc... is dissolved in a solvent like water, the electrolyte is completely dissociated to give its constituent ions (namely cations and anions). When an electric field is applied to such an electrolytic solution, the ions present in the solution carry charge from one electrode to another electrode and thereby they conduct electricity. The conductivity of the electrolytic solution is measured using a conductivity cell. (Fig 9.1)

A conductivity cell consists of two electrodes immersed in an electrolytic solution. It obeys Ohm's law like metallic conductor. i.e., at a constant temperature, the current flowing through the cell (I) is directly proportional to the voltage across the cell (V).

i.e., I
$$\alpha$$
 V (or) I = $\frac{V}{R} \Rightarrow$ V = IR(9.1)

Where 'R' is the resistance of the solution in ohm (Ω) Here the resistance is the opposition that a cell offers to the flow of electric current through it.



Resistivity (ρ)

Let us consider a conductivity cell in which the electrolytic solution is confined between the two electrodes having cross sectional area (A) and are separated by a distance l'. Like the metallic conductor, the resistance of such an electrolytic solution is also directly proportional to the length (l) and inversely proportional to the cross sectional area (A).

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

$$R = \rho \frac{l}{A}$$
(9.2)

Where ρ (rho) is called the specific resistance or resistivity, which depends on the nature of the electrolyte.

If $\frac{l}{A} = 1 \text{ m}^{-1}$, then, $\rho = R$. Hence the resistivity is defind as the resistance of an electrolyte confined between two electrodes having unit cross sectional area and are separated by a unit distance. The ratio $\int \frac{l}{r}$) is called the cell constant, Unit of resistivity is ohm metre (Ω m). Conductivity

It is more convenient to use conductance rather than resistance. The reciprocal of the gives the conductance of an resistance electrolytic solution. The SI unit of conductance is Siemen (S).

$$C = \frac{1}{R} \qquad \dots (9.3)$$

Substitude (R) from (9.2) in (9.3)

$$\Rightarrow$$
 i.e., $C = \frac{1}{\rho} \cdot \frac{A}{l}$ (9.4)



Fig 9.2 conductivity of a cube of an electrolytic solution

is called the specific conductance (or) The reciprocal of the specific resistance conductivity. It is represented by the symbol $\kappa_{appa}(\kappa)$.

Substitute
$$\frac{1}{\rho} = \kappa$$
 in equation (9.4) and rearranging
 $\Rightarrow \kappa = C. \left(\frac{l}{A}\right)$ (9.5)

Unit of
$$\kappa$$

 $\kappa = \frac{1}{R} \cdot \frac{l}{A} \left(\frac{1}{ohm} \cdot \frac{m}{m^2} \right)$
 $= ohm^{-1} m^{-1} = mho m^{-1} (or) Sm^{-1}$

If $A = 1m^2$ and l = 1m; then $\kappa = C$.

The specific conductance is defined as the conductance of a cube of an electrolytic solution of unit dimensions(Fig 9.2). The SI unit of specific conductance is Sm⁻¹.

Example

A conductivity cell has two platinum electrodes separated by a distance 1.5 cm and the cross sectional area of each electrode is 4.5 sq cm. Using this cell, the resistance of 0.5 N electrolytic solution was measured as 15 Ω . Find the specific conductance of the solution.

Solution

$$\kappa = \frac{1}{R} \left(\frac{l}{A} \right)$$

$$\kappa = \frac{1}{15\Omega} \times \frac{1.5 \times 10^{-2} \text{ m}}{4.5 \times 10^{-4} \text{ m}^2}$$

$$= 2.22 \text{ Sm}^{-1}$$

$$l = 1.5 \text{ cm} = 1.5 \times 10^{-2} \text{ m}$$

$$A = 4.5 \text{ cm}^2 = 4.5 \times (10^{-4}) \text{ m}^2$$

$$R = 15\Omega$$

9.1.1 Molar conductivity (Λ_m)

Solutions of different concentrations have different number of electrolytic ions in a given volume of solution and hence they have different specific conductance. Therefore a new quantity called molar conductance (Λ_m) was introduced.

Let us imagine a conductivity cell in which the electrodes are separated by 1m and having V m³ of electrolytic solution which contains 1 mole of electrolyte. The conductance of such a system is called the molar conductance (Λ_m)

We have just learnt that the conductance of 1 m³ electrolytic solution is called the specific conductance (κ). Therefore, the conductance of the above mentioned V m³ solution (Λ_m) is given by the following expression.

$$(\Lambda_{\rm m}) = \kappa \times V$$
(9.6)
Number of moles of solute (n)

We know that, molarity (M) =
$$\frac{1}{\text{Volume of the solution (V in dm}^3)}$$

Therefore, Volume of the solution containing one mole of solute = $\frac{1}{M}$ (mol⁻¹ L)

:. Volume per m³ (V) =
$$\frac{10}{M}$$
 (mol⁻¹m³
Substitute (9.7) in (9.6)

(9.6)
$$\Rightarrow \Lambda_{\rm m} = \frac{\kappa \,({\rm Sm}^{-1}) \times 10^{-3}}{{\rm M}} \,\,{\rm mol}^{-1}{\rm m}^{-3} \,\,....(9.8)$$

The above relation defines the molar conductance in terms of the specific conductance and the concentration of the electrolyte.

Example

Calculate the molar conductance of 0.025M aqueous solution of calcium chloride at 25°C. The specific conductance of calcium chloride is 12.04×10^{-2} Sm⁻¹.

Molar conductance =
$$\Lambda_{\rm m} = \frac{\kappa ({\rm Sm}^{-1}) \times 10^{-3}}{{\rm M}} {\rm mol}^{-1} {\rm m}^{3}$$

= $\frac{(12.04 \times 10^{-2} {\rm Sm}^{-1}) \times 10^{-3} ({\rm mol}^{-1} {\rm m}^{3})}{0.025}$
= $481.6 \times 10^{-5} {\rm Sm}^{2} {\rm mol}^{-1}$

Evaluate yourself : 1

Calculate the molar conductance of 0.01M aqueous KCl solution at 25°C. The specific conductance of KCl at 25°C is 14.114×10^{-2} Sm⁻¹.

9.1.2 Equivalent conductance (Λ)

Equivalent conductance is defined as the conductance of 'V' m³ of electrolytic solution containing one gram equivalent of electrolyte in a conductivity cell in which the electrodes are one metre apart.

The relation between the equivalent conductance and the specific conductance is given below.

$$\Lambda = \frac{\kappa (\mathrm{Sm}^{-1}) \times 10^{-3} (\mathrm{gram \ equivalent})^{-1} \mathrm{m}^3}{\mathrm{N}} \qquad \dots (9..9)$$

Where κ the specific conductance and N is the concentration of the electrolytic solution expressed in normality.

Evaluate yourself : 2

The resistance of 0.15N solution of an electrolyte is 50 Ω . The specific conductance of the solution is 2.4 Sm⁻¹. The resistance of 0.5 N solution of the same electrolyte measured using the same conductivity cell is 480 Ω . Find the equivalent conductivity of 0.5 N solution of the electrolyte.

Given that

$$\begin{split} R_1 &= 50 \ \Omega & R_2 &= 480 \ \Omega \\ \kappa_1 &= 2.4 \ \mathrm{Sm}^{-1} & \kappa_2 &= ? \\ N_1 &= 0.15 \ \mathrm{N} & N_2 &= 0.5 \ \mathrm{N} \\ \Lambda &= \frac{\kappa_2 \ (\mathrm{Sm}^{-1}) \times 10^{-3} \ (\mathrm{gram \ equivalent})^{-1} \ \mathrm{m}^3}{\mathrm{N}} & \mathrm{we \ know \ that} \\ &= \frac{0.25 \times 10^{-3} \ \mathrm{S} \ (\mathrm{gram \ equivalent})^{-1} \ \mathrm{m}^2}{0.5} & \kappa &= \frac{\mathrm{Cell \ constant}}{\mathrm{R}} \\ \Lambda &= 5 \times 10^{-4} \ \mathrm{Sm}^2 \ \mathrm{gram \ equivalent}^{-1} & \ddots \ \frac{\kappa_2}{\kappa_1} &= \frac{\mathrm{R}_1}{\mathrm{R}_2} \\ & \kappa_2 &= \kappa_1 \times \frac{\mathrm{R}_1}{\mathrm{R}_2} \\ & = 2.4 \ \mathrm{Sm}^{-1} \times \frac{50 \ \Omega}{480 \ \Omega} \\ &= 0.25 \ \mathrm{Sm}^{-1} \end{split}$$

9.1.3 Factors affecting electrolytic conductance

If the interionic attraction between the oppositely charged ions of solutes increases, the conductance will decrease.

- Solvent of higher dielectric constant show high conductance in solution.
- Conductance is inversely proportional to the Viscosity of the medium. i.e., conductivity increases with the decrease in viscosity.
- If the temperature of the electrolytic solution increases, conductance also increases. Increase in temperature increases the kinetic energy of the ions and decreases the attractive force between the oppositely charged ions and hence conductivity increases.
- Molar conductance of a solution increases with increase in dilution. This is because, for a strong electrolyte, interionic forces of attraction decrease with dilution. For a weak electrolyte, degree of dissociation increases with dilution.

9.1.4 Measurement of conductivity of ionic solutions

We have already learnt to measure the specific resistance of a metallic wire using a metre bridge in your physics practical experiment. We know that it works on the principle of wheatstone bridge. Similarly, the conductivity of an electrolytic solution is determined by using a wheatstone bridge arrangement in which one resistance is replaced by a conductivity cell filled with the electrolytic solution of unknown conductivity.

In the measurement of specific resistance of a metallic wire, a DC power supply is used. Here, if we apply DC current through the conductivity cell, it will lead to the electrolysis of the solution taken in the cell. So, AC current is used for this measurement to prevent electrolysis.

A wheatstone bridge is constituted using known resistances P, Q, a variable resistance S and conductivity cell (Let the resistance of the electrolytic solution



taken in it be R) as shown in the figure 9.3. An AC source (550 Hz to 5 KHz) is connected between the junctions A and C. Connect a suitable detector E (Such as the telephone ear piece detector) between the junctions 'B' and 'D'.

The variable resistance 'S' is adjusted until the bridge is balanced and in this conditions there is no current flow through the detector.

Under balanced condition,

$$\frac{P}{Q} = \frac{R}{S}$$
$$\therefore R = \frac{P}{Q} \times S$$

.....(9.10)

The resistance of the electrolytic solution (R) is calculated from the known resistance values P, Q and the measured 'S' value under balanced condition using the above expression (9.10).

Conductivity calculation

Specific conductance (or) conductivity of an electrolyte can be calculated from the resistance value using the following expression.

$$\kappa = \frac{1}{R} \left(\frac{l}{A} \right) \qquad [\because \text{ equation 9.5}]$$

The value of the cell constant $\frac{l}{A}$ is usually provided by the cell manufacturer. Alternatively the cell constant may be determined using KCl solution whose concentration and specific conductance are known.

Example

The resistance of a conductivity cell is measured as 190 Ω using 0.1M KCl solution (specific conductance of 0.1M KCl is 1.3 Sm⁻¹). When the same cell is filled with 0.003M sodium chloride solution, the measured resistance is 6.3K Ω . Both these measurements are made at a particular temperature. Calculate the specific and molar conductance of NaCl solution.

Given that

$$\kappa = 1.3 \text{ Sm}^{-1} \text{ (for 0.1M KCl solution)}$$

$$R = 190 \Omega$$

$$\left(\frac{l}{A}\right) = \kappa \cdot R = (1.3 \text{ Sm}^{-1}) (190 \Omega)$$

$$= 247 \text{ m}^{-1}$$

$$\kappa_{\text{(NaCl)}} = \frac{1}{R_{\text{(NaCl)}}} \left(\frac{l}{A}\right)$$

$$= \frac{1}{6.3 \text{ K}\Omega} (247 \text{ m}^{-1})$$

$$= 39.2 \times 10^{-3} \text{ Sm}^{-1}$$

$$\Lambda_{\text{m}} = \frac{\kappa \times 10^{-3} \text{ mol}^{-1} \text{ m}^{3}}{M}$$

$$= \frac{39.2 \times 10^{-3} (\text{Sm}^{-1}) \times 10^{-3} (\text{mol}^{-1}\text{m}^{3})}{0.003}$$

$$\Lambda_{\text{m}} = 13.04 \times 10^{-3} \text{ Sm}^{2} \text{ mol}^{-1}$$

9.2 Variation of molar conductivity with concentration

Friedrich Kohlraush studied the molar conductance of different electrolytes at different concentrations. He observed that, increase of the molar conductance of an electrolytic solution with the increase in the dilution. One such experimental results is given in the following table for better understanding.

Concentration	Molar conductance (×10 ⁻³ Sm ² mol ⁻¹)					
(M)	NaCl	KCl	HCl			
0.1	10.674	12.896	39.132			
0.01	11.851	14.127	41.20			
0.0001	12.374	14.695	42.136			

Based on the above such results, Kohlraush deduced the following empirical relationship between the molar conductance (Λ_m) and the concentration of the electrolyte (C).

The above equation represents a straight line of the form y = mx + c. Hence, the plot of Λ_m Vs \sqrt{C} gives a straight line with a negative slope of -k and the y intercept, Λ_m° . Where Λ_m° is called the limiting molar conductivity. i.e., the molar conductance approaches a limiting value in very dilute solutions.

For strong electrolytes such as KCl, NaCl etc., the plot, Λ_m Vs \sqrt{C} , gives a straight line as shown in the graph (9.4). It is also observed that the plot is not a linear one for weak electrolytes.

For a strong electrolyte, at high concentration, the number of constituent ions of the electrolyte in a given volume is high and hence the attractive force between the oppositely charged ions is also high. Moreover the ions also experience a viscous drag due to greater solvation. These factors attribute for the low molar conductivity at high concentration. When the dilution increases, the ions are far apart and the attractive forces decrease.



At infinite dilution the ions are so far apart, the interaction between them becomes insignificant and hence, the molar conductivity increases and reaches a maximum value at infinite dilution.

For a weak electrolyte, at high concentration, the plot is almost parallel to concentration axis with slight increase in conductivity as the dilution increases. When the concentration approaches zero, there is a sudden increase in the molar conductance and the curve is almost parallel to Λ_m axis. This is due to the fact that the dissociation of the weak electrolyte increases with the increase in dilution (Ostwald dilution law). Λ_m^0 values for strong electrolytes can be obtained by extrapolating the straight line, as shown in figure (9.4). But the same procedure is not applicable for weak electrolytes, as the plot is not a linear one, Λ_m^0 values of the weak electrolytes can be determined using Kohlraush's law.

9.2.1 Debye - Huckel and Onsager equation

We have learnt that at infinite dilution, the interaction between the ions in the electrolyte solution is negligible. Except this condition, electrostatic interaction between the ions alters the properties of the solution from those expected from the free – ions value. The influence of ion-ion interactions on the conductivity of strong electrolytes was studied by Debye and Huckel. They considered that each ion is surrounded by an ionic atmosphere of opposite sign, and derived an expression relating the molar conductance of strong electrolytes with the concentration by assuming complete dissociation. Later, the equation was further developed by Onsager. For a uni – univalent electrolyte the Debye Huckel and Onsager equation is given below.

Where A and B are the constants which depend only on the nature of the solvent and temperature. The expression for A and B are

A =
$$\frac{82.4}{\sqrt{DT} \eta}$$
; B = $\frac{8.20 \times 10^5}{\sqrt[3]{DT}}$

Here, D is the dielectric constant of the medium, η the viscosity of the medium and T the temperature in Kelvin.

9.2.2 Kohlraush's law

The limiting molar conductance Λ_m^0 is the basis for kohlraush law. At infinite dilution, the limiting molar conductivity of an electrolyte is equal to the sum of the limiting molar conductivities of its constituent ions. i.e., the molar conductivity is due to the independent migration of cations in one direction and anions in the opposite direction.

For a uni – univalent electrolyte such as NaCl, the Kohlraush's law is expressed as

$$\left(\Lambda_{m}^{0}\right)_{NaCl} = \left(\lambda_{m}^{0}\right)_{Na^{+}} + \left(\lambda_{m}^{0}\right)_{Cl}$$

In general, according to Kohlraush's law, the molar conductivity at infinite dilution for a electrolyte represented by the formula $A_x B_y$, is given below.

$$\left(\Lambda_{m}^{0}\right)_{A_{x}B_{y}} = x\left(\lambda_{m}^{0}\right)_{A^{y+}} + y\left(\lambda_{m}^{0}\right)_{B^{x-}} \qquad \dots (9.13)$$

Kohlraush arrived the above mentioned relationship based on the experimental observations such as the one as shown in the table. These result show that at infinite dilution each constituent ion of the electrolyte makes a definite contribution towards the molar conductance of the electrolyte irrespective of nature of other ion with which it is associated

$\left(\Lambda_{\rm m}^{\circ}\right)_{\rm KCl} - \left(\Lambda_{\rm m}^{\circ}\right)_{\rm NaCl} = 149.86 - 126.45$
$\left\{ \left(\lambda_{m}^{\circ}\right)_{K^{+}} + \left(\lambda_{m}^{\circ}\right)_{Cl^{-}} \right\} - \left\{ \left(\lambda_{m}^{\circ}\right)_{Na^{+}} + \left(\lambda_{m}^{\circ}\right)_{Cl^{-}} \right\} = 23.41$
$\left(\lambda_{m}^{\circ}\right)_{K^{+}}$ - $\left(\lambda_{m}^{\circ}\right)_{Na^{+}}$ = 23.41
Similarly, we can conclude that $(\lambda_m^\circ)_{Br^-} - (\lambda_m^\circ)_{Cl^-} = 2.06$

i.e.,

Applications of Kohlrausch's Law1. Calculation of molar conductance at infinite dilution of a weak electrolyte.

It is impossible to determine the molar conductance at infinite dilution for weak electrolytes experimentally. However, the same can be calculated using Kohlraush's Law.

For example, the molar conductance of CH₃COOH, can be calculated using the experimentally determined molar conductivities of strong electrolytes HCl, NaCl and CH₃COONa.

$$\Lambda^{\circ}_{CH_{3}COONa} = \lambda^{\circ}_{Na^{+}} + \lambda^{\circ}_{CH_{3}COO^{-}} \qquad \dots \dots (1)$$
$$\Lambda^{\circ}_{HCl} = \lambda^{\circ}_{H^{+}} + \lambda^{\circ}_{Cl^{-}} \qquad \dots \dots (2)$$
$$\Lambda^{\circ}_{A} = \lambda^{\circ}_{A} + \lambda^{\circ}_{A} \qquad \dots \dots (3)$$

$$\begin{pmatrix} \Lambda^{\circ}_{CH_{3}COONa} \end{pmatrix} + \begin{pmatrix} \Lambda^{\circ}_{HCl} \end{pmatrix} - \begin{pmatrix} \Lambda^{\circ}_{NaCl} \end{pmatrix} = \lambda^{\circ}_{H^{+}} + \lambda^{\circ}_{CH_{3}COO^{-}}$$
$$= \Lambda^{\circ}_{CH_{3}COOH}$$

2. Calculation of degree of dissociation of weak electrolytes

The degree of dissociation of weak electrolyte can be calculated from the molar conductivity at a given concentration and the molar conductivity at infinite dilution using the following expression

Calculation of dissociation constant using Λ_m values. According to Ostwald dilution Law,

$$K_a = \frac{\alpha^2 C}{(1-\alpha)} \qquad \dots (9.15)$$

Substitute α value in the above expression (9.15)

$$K_{a} = \frac{\Lambda_{m}^{2} C}{\Lambda_{m}^{o^{2}} \left(1 - \frac{\Lambda_{m}}{\Lambda_{m}^{o}}\right)}$$

Electrolyte	$\Lambda_{\rm m}^0$ at 298 K	Difference
KCl	149.86	
NaCl	126.45	23.41
KBr	151.92	
NaBr	128.51	23.41
KNO3	114.96	
NaNO ₃	121.55	23.41

Electrolyte	Λ_m^0 at 298 K	Difference
KBr	151.92	
KCl	149.86	2.06
NaBr	128.51	
NaCl	126.45	2.06
LiBr	117.09	
LiCl	115.03	2.06

$$K_{a} = \frac{\Lambda_{m} C}{\Lambda_{m}^{\circ 2} \frac{(\Lambda_{m}^{\circ} - \Lambda_{m})}{\Lambda_{m}^{\circ}}}$$

$$\Rightarrow K_{a} = \frac{\Lambda_{m}^{2} C}{\Lambda_{m}^{\circ} (\Lambda_{m}^{\circ} - \Lambda_{m})} \qquad \dots (9.16)$$

3. Calculation of solubility of sparingly soluble salts

Substances like AgCl, PbSO₄ etc., are sparingly soluble in water. The solubility product of such substances can be determined using conductivity measurements.

Let us consider AgCl as an example

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$$AgCl (s) \rightleftharpoons Ag^{+} + Cl^{-}$$
$$K_{sp} = [Ag^{+}][Cl^{-}]$$

Let the concentration of $[Ag^+]$ be 'C' molL⁻¹.

As per the stoichiometry, if $[Ag^+] = C$, then $[Cl^-]$ also equal to 'C' mol L^- .

$$K_{sp} = C.C$$

 $\Rightarrow K_{sp} = C$

We know that the concentration (in mol dm⁻³) is related to the molar and specific conductance by the following expressions

$$\Lambda_{o} = \frac{\kappa \times 10^{-3}}{C \text{ (in mol } L^{-1})}$$

(or)
$$C = \frac{\kappa \times 10^{-3}}{\Lambda^{\circ}}$$

Substitute the concentration value in the relation $K_{sp} = C^2$

$$K_{sp} = \left(\frac{\kappa \times 10^{-3}}{\Lambda^{\circ}}\right)^2 \qquad \dots (9.17)$$

9.3 Electrochemical Cell

Electrochemical cell is a device which converts chemical energy into electrical energy and vice versa. It consists of two separate electrodes which are in contact with an electrolyte solution. Electrochemical cells are mainly classified into the following two types.

- 1. **Galvanic Cell (Voltaic cell)** : It is a device in which a spontaneous chemical reaction generates an electric current i.e., it converts chemical energy into electrical energy. It is commonly known as a battery.
- 2. **Electrolytic cell** : It is a device in which an electric current from an external source drives a nonspontaneous reaction i.e., it converts electrical energy into chemical energy.

9.3.1 Galvanic cell

We have already learnt in XI standard that when a zinc metal strip is placed in a copper sulphate solution, the blue colour of the solution fades and the copper is deposited on the zinc strip as red – brown crust due to the following spontaneous chemical reaction.

 $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

The energy produced in the above reaction is lost to the surroundings as heat.

In the above redox reaction, Zinc is oxidised to Zn^{2+} ions and the Cu^{2+} ions are reduced to metallic copper. The half reactions are represented as below.

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ (oxidation) $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ (reduction)

If we perform the above two half reactions separately in an apparatus as shown in figure 9.5, some of the energy produced in the reaction will be converted into electrical energy. Let us understand the function of a galvanic cell by considering Daniel cell as an example. It uses the above reaction for generation of electrical energy.

The separation of half reaction is the basis for the construction of Daniel cell. It consists of two half cells.

Oxidation half cell

A metallic zinc strip that dips into an aqueous solution of zinc sulphate taken in a beaker, as shown in Figure 9.5.

Reduction half cell

A copper strip that dips into an aqueous solution of copper sulphate taken in a beaker, as shown in Figure 9.5.

Joining the half cells

The zinc and copper strips are externally connected using a wire through a switch (k) and a load (example: volt meter). The electrolytic solution present in the cathodic and anodic compartment are connected using an inverted U tube containing agar-agar gel mixed with an inert electrolytes such as KCl, Na₂SO₄ etc., The ions of inert electrolyte do not react with other ions present in the half cells and they are not either oxidised (or) reduced at the electrodes. The solution in the salt bridge cannot get poured out, but through which the ions can move into (or) out of the half cells.

When the switch (k) closes the circuit, the electrons flows from zinc strip to copper strip. This is due to the following redox reactions which are taking place at the respective electrodes.

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Anodic oxidation

The electrode at which the oxidation occurs is called the anode. In Daniel cell, the oxidation take place at zinc electrode, i.e., zinc is oxidised to Zn^{2+} ions by loosing its electrons. The Zn^{2+} ions enter the solution and the electrons enter the zinc metal, then flow through the external wire and then enter the copper strip. Electrons are liberated at zinc electrode and hence it is negative (- ve).

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-1}$$
 (loss of electron-oxidation)

Cathodic reduction

As discussed earlier, the electrons flow through the circuit from zinc to copper, where the Cu^{2+} ions in the solution accept the electrons, get reduced to copper and the same get deposited on the electrode. Here, the electrons are consumed and hence it is positive (+ve).

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$$\operatorname{Cu}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Cu}(s)$$

(gain of electron-reduction)



Salt bridge

The electrolytes present in two half cells are connected using a salt bridge. We have learnt that the anodic oxidation of zinc electrodes results in the increase in concentration of Zn^{2+} in solution. i.e., the solution contains more number of Zn^{2+} ions as compared to SO_4^{2-} and hence the solution in the anodic compartment would become positively charged. Similarly, the solution in the cathodic compartment would become negatively charged as the Cu^{2+} ions are reduced to copper i.e., the cathodic solution contain more number of SO_4^{2-} ions compared to Cu^{2+} .

To maintain the electrical neutrality in both the compartments, the non reactive anions Cl⁻ (from KCl taken in the salt bridge) move from the salt bridge and enter into the anodic compartment, at the same time some of the K⁺ ions move from the salt bridge into the cathodic compartment.

Completion of circuit

Electrons flow from the negatively charged zinc anode into the positively charged copper cathode through the external wire, at the same time, anions move towards anode and cations are move towards the cathode compartment. This completes the circuit.

Consumption of Electrodes

As the Daniel cell operates, the mass of zinc electrode gradually decreases while the mass of the copper electrode increases and hence the cell will function until the entire metallic zinc electrode is converted in to Zn^{2+} or the entire Cu^{2+} ions are converted in to metallic copper.

Unlike Daniel cell, in certain cases, the reactants (or) products cannot serve as electrodes and in such cases inert electrode such as graphite (or) platinum is used which conducts current in the external circuit.

9.3.2 Galvanic cell notation

The galvanic cell is represented by a cell diagram, for example, Daniel cell is represented as

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)||Cu(s)|$$

In the above notation, a single vertical bar (|) represents a phase boundary and the double vertical bar (||) represents the salt bridge.

The anode half cell is written on the left side of the salt bridge and the cathode half cell on the right side.

The anode and cathode are written on the extreme left and extreme right, respectively.

The emf of the cell is written on the right side after cell diagram.



Example

The net redox reaction of a galvanic cell is given below

 $2 \operatorname{Cr}(s) + 3\operatorname{Cu}^{2+}(aq) \rightarrow 2\operatorname{Cr}^{3+}(aq) + 3\operatorname{Cu}(s)$

Write the half reactions and describe the cell using cell notation.

Anodic oxidation $2Cr(s) \rightarrow 2Cr^{3+}(aq) + 6e^{-1}$ (1)

Cathodic reduction : $3Cu^{2+}$ (aq) + $6e^{-} \rightarrow 3Cu$ (s)(2)

Cell Notation is

 $Cr(s)|Cr^{3+}(aq)||Cu^{2+}(aq)|Cu(s)|$

9.3.3 emf of a Cell

We have learnt that when two half cells of a Daniel cell are connected, a spontaneous redox reaction will take place which results in the flow of electrons from anode to cathode. The force that pushes the electrons away from the anode and pulls them towards cathode is called the electromotive force (emf) (or) the cell potential. The SI unit of cell potential is the volt (v).

When there is one volt difference in electrical potential between the anode and cathode, one joule of energy is released for each columb of charge that moves between them.

i.e.,
$$IJ = IC \times IV$$
(9.18)

The cell voltage depends on the nature of the electrodes, the concentration of the electrolytes and the temperature at which the cell is operated. For example

At, 25°C, The emf of the below mentioned Daniel cell is 1.107 Volts

$$Zn(s)|Zn^{2+}(aq,1M)||Cu^{2+}(aq,1M)|Cu(s)$$
 $E^{0} = 1.107 V$

9.3.4 Measurement of electrode potential

The overall redox reaction can be considered as the sum of two half reactions i.e., oxidation and reduction. Similarly, the emf of a cell can be considered as the sum of the electrode potentials at the cathode and anode,

 $E_{cell} = (E_{ox})_{anode} + (E_{red})_{cathode} \qquad(9.19)$ Here, $(E_{ox})_{anode}$ represents the oxidation potential at anode and $(E_{red})_{cathode}$ represents the reduction potential at cathode. It is impossible to measure the emf of a single electrode, but we can measure the potential difference between the two electrodes (E_{cell}) using a voltmeter. If we know the emf of any one of the electrodes which constitute the cell, we can calculate the emf of the other electrode from the measured emf of the cell using the expression (9.19). Hence, we need a reference electrode whose emf is known

For that purpose, Standard Hydrogen Electrode (**SHE**) is used as the reference electrode. It has been assigned an arbitrary emf of exactly zero volt. It consists of a platinum electrode in contact with 1M HCl solution and 1 atm hydrogen gas. The hydrogen gas is bubbled through the solution at 25°C as shown in the figure 9.6. SHE can act as a cathode as well as an anode. The Half cell reactions are given below.

If SHE is used as a cathode, the reduction reaction is $2H^+(aq,1M)+2e^- \rightarrow H_2(g, 1 \text{ atm})$ $E^\circ = 0 \text{ volt}$ If SHE is used as an anode, the oxidation reaction is $H_2(g,1 \text{ atm}) \rightarrow 2H^+(aq, 1M) + 2e^ E^\circ = 0 \text{ volt}$



Illustration

Let us calculate the reduction potential of zinc electrode dipped in zinc sulphate solution using SHE.

Step: 1 The following galvanic cell is constructed using SHE

 $Zn\left(s\right)\left|\begin{array}{c}Zn^{_{2+}}\left(aq,\,1M\right)\right|\right| \; H^{_{+}}\left(aq,\,1M\right)\left|H_{_{2}}\left(g,\,1atm\right)\right| \; Pt\left(s\right)$

Step : 2 The emf of the above galvanic cell is measured using a volt meter. In this case, the measured emf of the above galvanic cell is 0.76V.

Calculation

We know that,

$$E_{cell}^{\circ} = \left(E_{ox}^{\circ}\right)_{Zn|Zn^{2+}} + \left(E_{red}^{\circ}\right)_{SHE}$$
 [From equation (9.19)]
$$E_{cell}^{\circ} = 0.76 \text{ and } \left(E_{red}^{\circ}\right)_{SHE} = 0V.$$
 Substitute these values in the above equation



$$\Rightarrow 0.76V = (E_{ox}^{\circ})_{zn|Zn^{2+}} + 0V$$

 $\Rightarrow (E_{ox}^{\circ})_{zn|Zn^{2+}} = 0.76V$

This oxidation potential corresponds to the below mentioned half cell reaction which takes place at the cathode.

 $Zn \rightarrow Zn^{2+} + 2e^{-}$ (Oxidation)

The emf for the reverse reaction will give the reduction potential

 $Zn^{2+}+2e^{-} \rightarrow Zn$; $E^{\circ} = -0.76V$

IUPAC definition

Electrode potential (E)

Electromotive force of a cell in which the electrode on the left is a standard hydrogen electrode and the electrode on the right is the electrode in question.

Standard electrode potential, E

The value of the standard emf of a cell in which molecular hydrogen under standard pressure is oxidised to solvated protons at the left hand electrode.

Evaluate yourself

1. The emf of the following cell at 25°C is equal to 0.34v. Calculate the reduction potential of copper electrode.

Pt (s) | H₂ (g, 1atm) | H⁺(aq, 1M) | Cu²⁺(aq, 1M) | Cu (s)

Using the calculated emf value of zinc and copper electrode, calculate the emf of the following cell at 25°C.

Zn(s) $Zn^{2+}(aq, 1M)$ $Cu^{2+}(aq, 1M)$ Cu(s)

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: $(E_{red}^{\circ^{\circ}})_{Zn^{2+}|Zn} = -0.76V.$

Evaluate yourself

Write the overall redox reaction which takes place in the galvanic cell,

 $Pt(s)|Fe^{2+}(aq),Fe^{3+}(aq)||MnO_{4}^{-}(aq),H^{+}(aq),Mn^{2+}(aq)|Pt(s)|$

9.4 Thermodynamics of cell reactions

We have just learnt that in a galvanic cell, the chemical energy is converted into electrical energy. The electrical energy produced by the cell is equal to the product of the total charge of electrons and the emf of the cell which drives these electrons between the electrodes.

If 'n' is the number of moles of electrons exchanged between the oxidising and reducing agent in the overall cell reaction, then the electrical energy produced by the cell is given as below.

Electrical energy = Charge of 'n' mole of electrons $\times E_{cell}$ (9.20)

Charge of 1 mole of electrons = one Faraday (1F)

 \therefore Charge of 'n' mole of electrons = nF

Equation (9.20)
$$\Rightarrow$$
 Electrical energy = nFE_{cell}(9.21)
Charge of one elctron = 1.602×10^{-19} C
 \therefore Charge one mole of elctron = $6.023 \times 10^{23} \times 1.602 \times 10^{-19}$ C
= 96488 C
i.e., 1F \approx 96500 C

This energy is used to do the electric work. Therefore the maximum work that can be obtained from a galvanic cell is

$$(W_{max})_{cell} = -nFE_{cell} \qquad \dots (9.22)$$

Here the (-) sign is introduced to indicate that the work is done by the system on the surroundings.

We know from the Second Law of thermodynamics that the maximum work done by the system is equal to the change in the Gibbs free energy of the system.

i.e.,
$$W_{\text{max}} = \Delta G$$
(9.23)

From (9.22) and (9.23),

$$\Delta G = - nFE_{cell} \qquad \dots (9.24)$$

For a spontaneous cell reaction, the ΔG should be negative. The above expression (9.24) indicates that E_{cell} should be positive to get a negative ΔG value.

When all the cell components are in their standard state, the equation (9.24) becomes

$$\Delta G^{\circ} = - nFE^{\circ}_{cell} \qquad \dots (9.25)$$

We know that the standard free energy change is related to the equilibrium constant as per the following expression.

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$$\Delta G^{\circ} = - RT \ln K_{eq} \qquad \dots (9.26)$$

Comparing (9.25) and (9.26),

$$nFE_{cell}^{\circ} = RT \ln K_{eq}$$

$$\Rightarrow E_{cell}^{\circ} = \frac{2.303 RT}{nF} \log K_{eq} \qquad \dots (9.27)$$

9.4.1 Nernst equation

Nernst equation is the one which relates the cell potential and the concentration of the species involved in an electrochemical reaction. Let us consider an electrochemical cell for which the overall redox reaction is,

 $xA + yB \rightleftharpoons lC + mD$

The reaction quotient Q for the above reaction is given below

$$Q = \frac{[C]^{t} [D]^{m}}{[A]^{x} [B]^{y}} \dots (9.28)$$

We have already learnt that,

$$\Delta G = \Delta G^{\circ} + RT \ln Q \qquad \dots (9.29)$$

The Gibbs free energy can be related to the cell emf as follows [:: equation (9.24) and (9.25)]

$$\Delta G$$
 = - nFE_{cell}; ΔG° = - nFE^o_{cell}

Substitute these values and Q from (9.28) in the equation (9.29)

$$(9.29) \Rightarrow -nFE_{cell} = -nFE_{cell}^{\circ} + RT \ln \frac{[C]^{l}[D]^{m}}{[A]^{x} [B]^{y}} \qquad \dots (9.30)$$

Divide the whole equation (9.30) by (-nF)

$$(9.25) \Rightarrow E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln \frac{[C]^{l}[D]^{m}}{[A]^{x} [B]^{y}}$$

$$(or) E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log \frac{[C]^{l}[D]^{m}}{[A]^{x} [B]^{y}} \qquad \dots (9.31)$$

The above equation (9.31) is called the Nernst equation

At 25°C (298K), the above equation (9.31) becomes,

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303 \times 8.314 \times 298}{n(96500)} \log \frac{[C]^{l}[D]^{m}}{[A]^{x} [B]^{y}}$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^{l}[D]^{m}}{[A]^{x} [B]^{y}} \qquad \begin{bmatrix} \therefore R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \\ T = 298 \text{ K.} \\ 1 \text{ F} = 96500 \text{ C mol}^{-1} \end{bmatrix} \qquad \dots (9.32)$$

Let us calculate the emf of the following cell at 25°C using Nernst equation.

Cu (s) $|Cu^{2+}(0.25 \text{ aq, M})||Fe^{3+}(0.005 \text{ aq M})|Fe^{2+}(0.1 \text{ aq M})|Pt (s)|$

Given :
$$(E^{\circ})_{Fe^{3+}|Fe^{2+}} = 0.77V \text{ and } (E^{\circ})_{Cu^{2+}|Cu} = 0.34 \text{ V}$$

Half reactions are

$$\begin{array}{ll} Cu (s) \to Cu^{2+}(aq) + 2e^{-} & (1) \\ 2 \ Fe^{3+}(aq) + 2e^{-} \to 2Fe^{2+}(aq) & (2) \end{array}$$

the overall reaction is

Cu (s) + 2 Fe³⁺(aq)
$$\rightarrow$$
 Cu²⁺(aq) + 2 Fe²⁺ (aq), and n = 2

Apply Nernst equation at .25°C.

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{[Cu^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2} \qquad [:: [Cu (s)] = 1]$$
$$E_{cell}^{\circ} = (E_{ox}^{\circ})_{Cu|Cu^{2+}} + (E_{red}^{\circ})_{Fe^{3+}|Fe^{2+}}$$

Given standard reduction potential of Cu^{2+} Cu is 0.34V

$$\therefore (E_{ox}^{\circ})_{Cu|Cu|^{2^{2}}} = -0.34V$$

$$(E_{red}^{\circ})_{Fe^{2^{*}}}|_{Fe^{2^{*}}} = 0.77V$$

$$\therefore E_{cell}^{\circ} = -0.34 + 0.77$$

$$E_{cell}^{\circ} = 0.43V$$

$$\therefore E_{cell} = 0.43 - \frac{0.0591}{2} \times \log \frac{(0.25)(0.1)^{2}}{(0.005)^{2}}$$

$$= 0.43 - \frac{0.0591}{2} \times 2$$

$$= 0.43 - 0.0591$$

$$= 0.43 - 0.0591$$

$$= 0.3709V.$$

$$= -0.3709V.$$

$$= -0.34 + 0.77$$

$$= -0.34 + 0.77$$

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$$= -0.370 + 0.77$$

$$= -0.34 + 0.77$$

$$= -0.370 + 0.77$$

$$= -0.34 + 0.77$$

Evaluate yourself

The electrochemical cell reaction of the Daniel cell is

 $\mathrm{Zn}\ (s) + \mathrm{Cu}^{\scriptscriptstyle 2+}(\mathrm{aq})\ \rightarrow\ \mathrm{Zn}^{\scriptscriptstyle 2+}(\mathrm{aq}) + \mathrm{Cu}\ (s)$

What is the change in the cell voltage on increasing the ion concentration in the anode compartment by a factor 10?

Electrolytic cell and electrolysis

Electrolysis is a process in which the electrical energy is used to cause a non-spontaneous chemical reaction to occur; the energy is often used to decompose a compound into its elements. The device which is used to carry out the electrolysis is called the electrolytic cell. The electrochemical process occurring in the electrolytic cell and galvanic cell are the reverse of each other. Let us understand the function of a electrolytic cell by considering the electrolysis of molten sodium chloride.

The electrolytic cell consists of electrodes two one is cylindrical steel cathode and another one is graphite anode. They are dipped in molten sodium chloride. They are connected to the external DC power supply via a key as shown in the figure (9.8). The electrode which is attached to the negative end of the power supply is called the cathode, and the one which



attached to the positive end is called the anode. Once the key is closed, the external DC power supply drives the electrons to the cathode and at the same time pull the electrons from the anode.

Cell reactions

 Na^+ ions are attracted towards cathode, where they combine with the electrons and reduced to liquid sodium.

Cathode (reduction)

$$Na^+(l)+e^- \rightarrow Na(l)$$

Similarly, Cl⁻ ions are attracted towards anode where they lose their electrons and oxidised
to chlorine gas.
Anode (oxidation)

$$2Cl^{\circ}(l) \rightarrow Cl_{2}(g) + 2e^{-1} \qquad E^{\circ} = -1.36V$$

The overall reaction is,

 $2Na^{+}(l) + 2Cl^{-}(l) \rightarrow 2Na(l) + Cl_{2}(g)$ $E^{\circ} = -4.07V$

The negative E° value shows that the above reaction is a non spontaneous one. Hence, we have to supply a voltage greater than 4.07V to cause the electrolysis of molten NaCl.

In electrolytic cell, oxidation occurs at the anode and reduction occur at the cathode as in a galvanic cell, but the sign of the electrodes is the reverse i.e., in the electrolytic cell cathode is –ve and anode is +ve.

Faraday's Laws of electrolysis

First Law

The mass of the substance (m) liberated at an electrode during electrolysis is directly proportional to the quantity of charge (Q) passed through the cell.

i.e $m \alpha Q$

We know that the charge is related to the current by the equation $I = \frac{Q}{+} \Rightarrow Q = It$

 $\therefore m \alpha It$

m = Z It

(or)

..... (9.33)

Where is Z is known as the electro chemical equivalent of the substance produced of the electrode.

When, I = 1A and t = 1sec, Q = 1C, in such case the equation (9.32) becomes, (9.33) $\Rightarrow m = Z$ (9.34)

Thus, the electrochemical equivalent is defined as the amount of substance deposited or liberated at the electrode by a charge of 1 coulomb.

Electro chemical equivalent and molar mass

Consider the following general electrochemical redox reaction

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

We can infer from the above equation that 'n' moles of electrons are required to precipitate 1 mole of M^{n+} as M(s).

The quantity of charge required to precipitate one mole of M^{n+} = Charge of 'n' moles of electrons

= nF

In other words, the mass of substance deposited by one coulomb of charge

Electrochemical equivalent of
$$M^{n+} = \frac{\text{Molarmass of } M}{n (96500)}$$

(or)
 $Z = \frac{\text{Equivalent mass}}{96500}$ (9.35)

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When the same quantity of charge is passed through the solutions of different electrolytes, the amount of substances liberated at the respective electrodes are directly proportional to their electrochemical equivalents.

Let us consider three electrolytic cells connected in series to the same DC electrical source as shown in the figure 9.9. Each cell is filled with a different electrolytes namely $NiSO_4$, $CuSO_4$ and $CoSO_4$, respectively.

When Q coulomb charge is passed through the electrolytic cells the masses of Nickel, copper and cobalt deposited at the respective electrodes be m_{Ni} , m_{Cu} and m_{Co} , respectively.

According to Faraday's second Law,

$$m_{Ni} \alpha Z_{Ni}, m_{Cu} \alpha Z_{Cu} \text{ and } m_{Co} \alpha Z_{Co}$$
(or)
$$\frac{m_{Ni}}{Z_{Ni}} = \frac{m_{Cu}}{Z_{Cu}} = \frac{m_{Co}}{Z_{Co}}$$
.....(9.36)
Example

A solution of silver nitrate is electrolysed for 20 minutes with a current of 2 amperes. Calculate the mass of silver deposited at the cathode.

Electrochemical reaction at cathode is $Ag^++e^- \rightarrow Ag$ (reduction)

 $Z = \frac{\text{molarmass of Ag}}{(96500)} = \frac{108}{1 \times 96500}$ m = ZIt $\frac{108 \text{ gmol}^{-1}}{96500 \text{ C mol}^{-1}} \times 2400 \text{C}$ m = I = 2A $t = 20 \times 60S = 1200 S$ m = 2.68 g. $It = 2A \times 1200S = 2400C$

(55)

Evaluate yourself A solution of a salt of metal was electrolysed for 15 minutes with a current of 0.15 amperes. The mass of the metal deposited at the cathode is 0.783g. calculate the equivalent mass of the metal.

Batteries

Batteries are indispensable in the modern electronic world. For example, Li – ion batteries are used in cell phones, dry cell in flashlight etc.... These batteries are used as a source of direct current at a constant voltage. We can classify them into primary batteries (non – rechargeable) and secondary batteries (rechargeable). In this section, we will briefly discuss the electrochemistry of some batteries.

Leclanche cell

Anode : Zinc container

Cathode : Graphite rod in contact with MnO_2

Electrolyte : ammonium chloride and zinc chloride in water

Emf of the cell is about 1.5V

Cell reaction

Oxidation at anode

$$\operatorname{Zn}(s) \to \operatorname{Zn}^{2+}(\operatorname{aq})+2e^{-1}$$
(1)

Reduction at cathode

$$2 \operatorname{NH}_{4}^{+}(\operatorname{aq}) + 2e^{-} \rightarrow 2\operatorname{NH}_{3}(\operatorname{aq}) + \operatorname{H}_{2}(g) \qquad \dots (2)$$

The hydrogen gas is oxidised to water by MnO_2

$$H_2(g) + 2 MnO_2(s) \rightarrow Mn_2O_3(s) + H_2O(l)$$
(3)

Equation (1) + (2)+(3) gives the overall redox reaction



 $Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l) + 2NH_3$ (4)

Ammonia produced at the cathode combines with Zn^{2+} to form a complex ion $[Zn (NH_3)_4]^{2+}$ (aq). As the reaction proceeds, the concentration of NH_4^+ will decrease and the aqueous NH_3 will increase which lead to the decrease in the emf of cell. **Mercury button cell**

Anode	:	zinc amalgamated with mercury
Cathode	:	HgO mixed with graphite
Electrolyte	:	Paste of KOH and ZnO
Oxidation occurs at anode	:	$Z_{n}^{0}(s) + 2OH^{-}(aq) \rightarrow Z_{n}^{+2}O(s) + H_{2}O(l) + 2e^{-l}$
Reduction occurs at cathode	:	$\operatorname{HgO}(s) + \operatorname{H_2O}(l) + 2e^{-} \rightarrow \operatorname{Hg}(l) + 2OH^{-}(aq)$
Overall reaction	:	$Zn (s) + HgO (s) \rightarrow ZnO (s) + Hg (l)$
Cell emf	:	about 1.35V.
Uses	:	It has higher capacity and longer life. Used





Secondary batteries

We have already learnt that the electrochemical reactions which take place in a galvanic cell may be reversed by applying a potential slightly greater than the emf generated by the cell. This principle is used in secondary batteries to regenerate the original reactants. Let us understand the function of secondary cell by considering the lead storage battery as an example

Lead storage battery

Anode : spongy lead

Cathode : lead plate bearing PbO₂

Electrolyte : 38% by mass of H_2SO_4 with density 1.2g / mL.

Oxidation occurs at the anode

$$Pb(s) \rightarrow Pb^{2+}(aq)+2e^{-1}$$
(1)

The Pb²⁺ ions combine with SO_4^{-2} to form PbSO₄ precipitate.

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

Reduction occurs at the cathode

$$PbO_2(s) + 4 H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$$
(3)

The Pb^{2+} ions also combine with SO_4^{2-} ions from sulphuric acid to form $PbSO_4$ precipitate.

$$Pb^{2+} (aq) + SO_4^{2-} (aq) \rightarrow PbSO_4(s) \qquad \dots (4)$$

The Overall reactions is

Equation (1) + (2) + (3) + (4)

Pb (s) + PbO₂ (s) + 4H ⁺(aq) + 2SO₄²⁻ (aq) \rightarrow 2 PbSO₄ (s) + 2H₂O (l)

The emf of a single cell is about 2V . Usually six such cells are combined in series to produce 12volt

The emf of the cell depends on the concentration of H_2SO_4 . As the cell reaction uses SO_4^{2-} ions, the concentration H_2SO_4 decreases. When the cell potential falls to about 1.8V, the cell has to be recharged.

Recharge of the cell

As said earlier, a potential greater than 2V is applied across the electrodes, the cell reactions that take place during the discharge process are reversed. During recharge process, the role of anode and cathode is reversed and H_2SO_4 is regenerated.

Oxidation occurs at the cathode (now act as anode)

 $PbSO_4$ (s) + 2H₂O (l) $\rightarrow PbO_2$ (s) + 4 H⁺(aq) + SO₄²⁻ (aq) + 2e⁻

Reduction occurs at the anode (now act as cathode) $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2^-}(aq)$ Overall reaction

 $2PbSO_4 (s) + 2H_2O (l) \rightarrow Pb (s) + PbO_2 (s) + 4H^+(aq) + 2SO_4^{2-} (aq).$

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Thus, the overall cell reaction is exactly the reverse of the redox reaction which takes place while discharging.

Uses:

Used in automobiles, trains, inverters etc...

The lithium – ion Battery

- Anode : Porus graphite
- Cathode : transition metal oxide such as CoO_2 .



Electrolyte : Lithium salt in an organic solvent

At the anode oxidation occurs

 $\text{Li}(s) \rightarrow \text{Li}^+(aq) + e^{-\frac{1}{2}}$

At the cathode reduction occurs $\text{Li}^+ + \text{CoO}_2$ (s) + e⁻ \rightarrow Li CoO₂ (s)

> Overall reactions Li (s) + CoO₂ \rightarrow LiCoO₂ (s)

Both electrodes allow Li^+ ions to move in and out of their structures.

During discharge, the Li^+ ions produced at the anode move towards cathode through the non – aqueous electrolyte. When a potential greater than the emf produced by the cell is applied across the electrode, the cell reaction is reversed and now the Li^+ ions move from cathode to anode where they become embedded on the porous graphite electrode. This is known as intercalation.



Uses :

Used in cellular phones, laptops, computers, digital cameras, etc...

Fuel cell

The galvanic cell in which the energy of combustion of fuels is directly converted into electrical energy is called the fuel cell. It requires a continuous supply of reactant to keep functioning. The general representation of a fuel cell is follows

Fuel | Electrode | Electrolyte | Electrode | Oxidant

Let us understand the function of fuel cell by



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considering hydrogen – oxygen fuel cell. In this case, hydrogen act as a fuel and oxygen as an oxidant and the electrolyte is aqueous KOH maintained at 200°C and 20 – 40 atm. Porous graphite electrode containing Ni and NiO serves as the inert electrodes.

Hydrogen and oxygen gases are bubbled through the anode and cathode, respectively.

Oxidation occurs at the anode:

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

Reduction occurs at the cathode $O_2(g) + 2 H_2O(l) + 4e^- \rightarrow 4 OH^-(aq)$

The overall reaction is $_{2H_2}(g) + O_2(g) \rightarrow 2H_2O(l)$

The above reaction is the same as the hydrogen combustion reaction, however, they do not react directly ie., the oxidation and reduction reactions take place separately at the anode and cathode respectively. Like H_2 - O_2 fuel cell other fuel cells like propane $-O_2$ and methane O_2 have also been developed.

Corrosion

We are familiar with the rusting of iron. Have you ever noticed a green film formed on copper and brass vessels? In both, the metal is oxidised by oxygen in presence of moisture. This redox process which causes the deterioration of metal is called corrosion. As the corrosion of iron causes damages to our buildings, bridges etc....it is important to know the chemistry of rusting and how to prevent it. Rusting of iron is an electrochemical process.

Electrochemical mechanism of corrosion

The formation of rust requires both oxygen and water. Since it is an electrochemical redox process, it requires an anode and cathode in different places on the surface of iron. The iron surface and a droplet of water on the surface as shown in figure (9.15) form a tiny galvanic cell. The region enclosed by water is exposed to low amount of oxygen and it acts as the anode. The remaining area has high amount of oxygen and it acts as cathode. So based on the oxygen content, an electro chemical cell is formed. corrosion occurs at the anode i,e,. in the region enclosed by the water as discussed below.



At anode (oxidation): Iron dissolves in the anode region

 $2\text{Fe}(s) \rightarrow 2\text{Fe}^{2+}(aq)+4e^{-1}$ $E^{\circ} = 0.44\text{V}.$

The electrons move through the iron metal from the anode to the cathode area where the oxygen dissolved in water, is reduced to water.

At Cathode (reduction)

The reaction of atmospheric carbon dioxide with water gives carbonic acid which furnishes the H^+ ions for reduction.

 $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E^\circ = 1.23V$

The electrical circuit is completed by the migration of ions through water droplet.

The overall redox reactions is,

$$2Fe(s)+O_2(g)+4H^+(aq) \rightarrow 2Fe^{2+}(aq)+2H_2O(l)$$
 $E^\circ = 0.444+1.23=1.67V$

The positive emf value indicates that the reaction is spontaneous.

 Fe^{2+} ions are further oxidised to Fe^{3+} , which on further reaction with oxygen form rust. $4Fe^{2+}(aq)+O_2(g)+4H^+(aq) \rightarrow 4Fe^{3+}(aq)+2H_2O(l)$

$$2\mathrm{Fe}^{3+}(\mathrm{aq})+4\mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Fe}_{2}\mathrm{O}_{3}.\mathrm{H}_{2}\mathrm{O}(\mathrm{s})+6\mathrm{H}^{+}(\mathrm{aq})$$

Other metals such as aluminium, copper and silver also undergo corrosion, but at a slower rate than iron. For example, let us consider the reduction of aluminium,

$$Al(s) \rightarrow Al^{3+} (aq) + 3e^{-1}$$

 Al^{3+} , which reacts with oxygen in air to forms a protective coating of Al_2O_3 . This coating act as a protective film for the inner surface. So, further corrosion is prevented.

Protection of metals form corrosion

This can be achieved by the following methods.

- i. Coating metal surface by paint.
- ii. Galvanizing by coating with another metal such as zinc. zinc is stronger reducing agent than iron and hence it can be more easily corroded than iron. i.e., instead of iron, the zinc is oxidised.
- iii. Cathodic protection In this technique, unlike galvanising the entire surface of the metal to be protected need not be covered with a protecting metal. Instead, metals such as Mg or zinc which is corroded more easily than iron can be used as a sacrificial anode and the iron material acts as a cathode. So iron is protected, but Mg or Zn is corroded.

Passivation - The metal is treated with strong oxidising agents such as concentrated HNO₃. As a result, a protective oxide layer is formed on the surface of metal.

Alloy formation - The oxidising tendency of iron can be reduced by forming its alloy with other more anodic metals.

Example, stainless steel - an alloy of Fe and Cr.

Electrochemical series

We have already learnt that the standard single electrode potentials are measured using standard hydrogen electrode. The standard electrode potential at 298K for various metal - metal ion electrodes are arranged in the decreasing order of their standard reduction potential values as shown in the figure.

This series is called electrochemical series.

The standard reduction potential (E°) is a measure of the oxidising tendency of the species. The greater the E° value, greater is the tendency shown by the species to accept electrons and undergo reduction. So higher the (E°)

Half Reaction						Sta Po	ndard tential	(V)	
 C	H F_2 Cl_2 D_2+4H Ag^+ Fe^{3+} Cu^{2+} $2H^+$ Pb^{2+} Fe^{2+} Zn^{2+}	<u>+</u> + +	f R + + + + + + + + + + + + + +	eact 2e ⁻ 2e ⁻ 4e ⁻ 1e ⁻ 2e ⁻ 2e ⁻ 2e ⁻ 2e ⁻	ion # # # # # # # # # # #	2F ⁻ 2Cl ⁻ 2H ₂ C Ag Fe ²⁺ Cu H ₂ Pb Fe Zn	Point Stronger reducing agen	+2.87 +1.67 +1.36 +1.23 +0.80 +0.77 +0.34 0.00 -0.13 -0.44 -0.76	(<u>V</u>)
	Al ³⁺ Mg ²⁻ Li ⁺	F	+ + +	3e ⁻ 2e ⁻ 1e ⁻	11 11 11	AI Mg Li	V	-1.66 -2.36 -3.05	

Value, lesser is the tendency to undergo corrosion



Choose the correct answer:

- 1. The number of electrons that have a total charge of 9650 coulombs is
 - a) 6.22×10^{23}
 - c) 6.022×10^{22}
- 2. Consider the following half cell reactions:

 $Mn^{2+} + 2e^- \rightarrow Mn E^\circ = -1.18V$ $Mn^{2+} \rightarrow Mn^{3+} + e^- E^\circ = -1.51V$ c) 6.022×10^{-34}

b) 6.022×10^{24}



The E° for the reaction $3Mn^{2+} \rightarrow Mn+2Mn^{3+}$, and the possibility of the forward reaction are respectively.

- a) 2.69V and spontaneous b) -2.69 and non spontaneous
- c) 0.33V and Spontaneous d) 4.18V and non spontaneous
- 3. The button cell used in watches function as follows

 $\begin{array}{ll} Zn\left(s\right) + Ag_{2}O\left(s\right) + H_{2}O\left(l\right) \rightleftharpoons 2 Ag\left(s\right) + Zn^{2+}(aq) + 2OH^{-}\left(aq\right) & \text{the half cell} \\ \text{potentials are } Ag_{2}O\left(s\right) + H_{2}O\left(l\right) + 2e^{-} \rightarrow 2Ag\left(s\right) + 2 OH^{-}\left(aq\right) & E^{\circ} = 0.34V & \text{and} \\ Zn\left(s\right) \rightarrow Zn^{2+}(aq) + 2e^{-} & E^{0} = 0.76V & \text{The cell potential will be} \end{array}$

a) 0.84V b) 1.34V c) 1.10V d) 0.42V

- 4. The molar conductivity of a 0.5 mol dm⁻³ solution of AgNO₃ with electrolytic conductivity of 5.76×10^{-3} S cm⁻¹ at 298 K is
 - a) 2.88 S cm²mol⁻¹
 - c) $0.086 \text{ S cm}^2 \text{mol}^{-1}$

b) 11.52 S cm²mol⁻¹
d) 28.8 S cm²mol⁻¹

5.

Electrolyte	KCl	KNO ₃	HCl	NaOAC	NaCl
Λ_{-} (S cm ² mol ⁻¹)	149.9	145.0	426.2	91.0	126.5

Calculate Λ°_{HOAC} using appropriate molar conductances of the electrolytes listed above at infinite dilution in water at 25°C.

a) 517.2 b) 552.7 c) 390.7 d) 217.5

- 6. Faraday constant is defined as
 - a) charge carried by 1 electron
 - b) charge carried by one mole of electrons
 - c) charge required to deposit one mole of substance
 - d) charge carried by 6.22×10^{10} electrons.
- 7. How many faradays of electricity are required for the following reaction to occur $MnO_4^- \rightarrow Mn^{2+}$
 - a) 5F b) 3F c) 1F d) 7F
- 8. A current strength of 3.86 A was passed through molten Calcium oxide for 41minutes and 40 seconds. The mass of Calcium in grams deposited at the cathode is (atomic mass of Ca is 40g / mol and 1F = 96500C).
 - a) 4 b) 2
- 9. During electrolysis of molten sodium chloride, the time required to produce 0.1mole of chlorine gas using a current of 3A is

c) 8

- a) 55 minutes b) 107.2 minutes c) 220 minutes d) 330 minutes
- 10. The number of electrons delivered at the cathode during electrolysis by a current of 1A in 60 seconds is (charge of electron = 1.6×10^{-19} C)
 - a) 6.22×10^{23} b) 6.022×10^{20} c) 3.75×10^{20} d) 7.48×10^{23}
- 11. Which of the following electrolytic solution has the least specific conductance
 - a) 2N b) 0.002N c) 0.02N d) 0.2N
- 12. While charging lead storage battery
 - a) $PbSO_4$ on cathode is reduced to Pb b) $PbSO_4$ on anode is oxidised to PbO_2
 - c) $PbSO_4$ on anode is reduced to Pb
- d) PbSO₄ on cathode is oxidised to Pb

d) 6

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13. Among the following cells

I) Leclanche cell						
II) Nickel – Cadmium cell						
III) Lead storage l	oattery					
IV) Mercury cell						
Primary cells are						
a) I and IV	b) I and III	c) III and IV	d) II and III			

- 14. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because
 - a) Zinc is lighter than iron
 - b) Zinc has lower melting point than iron
 - c) Zinc has lower negative electrode potential than iron
 - d) Zinc has higher negative electrode potential than iron
- 15. Assertion : pure iron when heated in dry air is converted with a layer of rust. Reason : Rust has the composition Fe_3O_4
 - a) if both assertion and reason are true and reason is the correct explanation of assertion.
 - b) if both assertion and reason are true but reason is not the correct explanation of assertion.
 - c) assertion is true but reason is false
 - d) both assertion and reason are false.
- 16. In H_2 -O₂ fuel cell the reaction occurs at cathode is
 - a) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
 - b) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$
 - c) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$
 - d) $\mathrm{H^{+}} + \mathrm{e^{-}} \rightarrow \frac{1}{2} \mathrm{H_{2}}$
- 17. The equivalent conductance of $\frac{M}{36}$ solution of a weak monobasic acid is 6 mho cm² equivalent ⁻¹ and at infinite dilution is 400 mho cm² equivalent ⁻¹. The dissociation constant of this acid is
 - a) 1.25×10^{-6} b) 6.25×10^{-6} c) 1.25×10^{-4} d) 6.25×10^{-5}
- 18. A conductivity cell has been calibrated with a 0.01M, 1:1 electrolytic solution (specific conductance ($\kappa = 1.25 \times 10^{-3} \text{ S cm}^{-1}$) in the cell and the measured resistance was 800 Ω at 25°C. The cell constant is,

a) 10^{-1} c m⁻¹ b) 10^{1} c m⁻¹ c) 1 c m⁻¹ d) 5.7×10^{-12}

19. Conductivity of a saturated solution of a sparingly soluble salt AB (1:1 electrolyte) at 298K is 1.85×10^{-5} S m⁻¹. Solubility product of the salt AB at 298K $(\Lambda_{m}^{\circ})_{AB} = 14 \times 10^{-3}$ S m² mol⁻¹.

a) 5.7×10^{-12} b) 1.32×10^{-12} c) 7.5×10^{-12} d) 1.74×10^{-12}

20. In the electrochemical cell: $Zn|ZnSO_4 (0.01M)||CuSO_4(1.0M)||Cu, the emf of this Daniel cell is E₁. When the concentration of <math>ZnSO_4$ is changed to 1.0M and that $CuSO_4$ changed to 0.01M, the emf changes to E₂. From the above, which one is the relationship between E₁ and E₂?

a)
$$E_1 < E_2$$
 b) $E_1 > E_2$ c) $E_2 \ge E_1$ d) $E_1 = E_2$

21. Consider the change in oxidation state of Bromine corresponding to different emf values as shown in the diagram below:

 $BrO_{4}^{-} \xrightarrow{1.82V} BrO_{3}^{-} \xrightarrow{1.5V} HBrO \xrightarrow{1.595V} Br_{2} \xrightarrow{1.0652V} Br^{-}$ Then the species undergoing disproportionation is

a) Br_2 b) BrO_4^- c) BrO_3^- d) HBrO

22. For the cell reaction

 $2Fe^{3+}(aq) + 2l^{-}(aq) \rightarrow 2Fe^{2+}(aq) + l_2(aq)$

 $E_{cell}^{\circ} = 0.24V$ at 298K. The standard Gibbs energy (Δ , G°) of the cell reactions is :

a) -46.32 KJ mol⁺ b) -23.16 KJ mol⁺ c) 46.32 KJ mol⁺ d) 23.16 KJ mol⁺

23. A certain current liberated 0.504gm of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time through copper sulphate solution

- a) 31.75 b) 15.8 c) 7.5 d) 63.5
- 24. A gas X at 1 atm is bubbled through a solution containing a mixture of 1MY⁻ and 1MZ⁻ at 25°C. If the reduction potential of Z>Y>X, then
 - a) Y will oxidize X and not Z b) Y will oxidize Z and not X
 - d) Y will oxidize both X and Z d) Y will reduce both X and Z
- 25. Cell equation : $A + 2B^{-} \rightarrow A^{2+} + 2B;$

 $A^{2+} + 2e^- \rightarrow A$ $E^{\circ} = +0.34V$ and $\log_{10}K = 15.6$ at 300K for cell reactions find E° for $B^+ + e^- \rightarrow B$ (AIIMS – 2018)

a) 0.80 b) 1.26 c) -0.54 d) -10.94

Short Answer Questions

- 1. Define anode and cathode
- 2. Why does conductivity of a solution decrease on dilution of the solution
- 3. State Kohlrausch Law. How is it useful to determine the molar conductivity of weak electrolyte at infinite dilution.

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- 4. Describe the electrolysis of molten NaCl using inert electrodes
- 5. State Faraday's Laws of electrolysis
- 6. Describe the construction of Daniel cell. Write the cell reaction.
- 7. Why is anode in galvanic cell considered to be negative and cathode positive electrode?
- 8. The conductivity of a 0.01M solution of a 1 :1 weak electrolyte at 298K is 1.5×10^{-4} S cm⁻¹.

i) molar conductivity of the solution

ii) degree of dissociation and the dissociation constant of the weak electrolyte

Given that

 $\lambda^{\circ}_{cation} = 248.2 \text{ S cm}^2 \text{ mol}^{-1}$

 $\lambda_{anion}^{\circ} = 51.8 \text{ S cm}^2 \text{ mol}^{-1}$

- 9. Which of 0.1M HCl and 0.1 M KCl do you expect to have greater Λ_m and why?
- 10. Arrange the following solutions in the decreasing order of specific conductance.

i) 0.01M KCl	ii) 0.005M KCl	iii) 0.1M KCl

iv) 0.25 M KCl v) 0.5 M KCl

- 11. Why is AC current used instead of DC in measuring the electrolytic conductance?
- 12.0.1M NaCl solution is placed in two different cells having cell constant 0.5 and 0.25cm⁻¹ respectively. Which of the two will have greater value of specific conductance.
- 13. A current of 1.608A is passed through 250 mL of 0.5M solution of copper sulphate for 50 minutes. Calculate the strength of Cu²⁺ after electrolysis assuming volume to be constant and the current efficiency is 100%.
- 14. Can Fe³⁺ oxidises bromide to bromine under standard conditions?

Given: $E^{\circ}_{Fe^{3+}|Fe^{2+}} = 0.771$ $E^{\circ}_{Br,|Br^{-}} = 1.09V.$

15. Is it possible to store copper sulphate in an iron vessel for a long time?

Given : $E^{\circ}_{Cu^{2+}|Cu} = 0.34 \text{ V} \text{ and } E^{\circ}_{Fe^{2+}|Fe} = -0.44 \text{ V}$.

- 16. Two metals M_1 and M_2 have reduction potential values of -xV and +yV respectively. Which will liberate H_2 and H_2SO_4 .
- 17. Reduction potential of two metals M_1 and M_2 are $E^{\circ}_{M_1^{2^+}|M_1} = -2.3V$ and $E^{\circ}_{M_1^{2^+}|M_2} = 0.2V$ Predict which one is better for coating the surface of iron. Given : $E^{\circ}_{E^{2^+}|E_{e}} = -0.44V$
- 18. Calculate the standard emf of the cell: $Cd|Cd^{2+}||Cu^{2+}|Cu$ and determine the cell reaction. The standard reduction potentials of $Cu^{2+}|Cu$ and $Cd^{2+}|Cd$ are 0.34V and -0.40 volts respectively. Predict the feasibility of the cell reaction.

- 19. In fuel cell H_2 and O_2 react to produce electricity. In the process, H_2 gas is oxidised at the anode and O_2 gas is reduced at cathode. If 44.8 litre of H_2 at 25°C and 1atm pressure reacts in 10 minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu²⁺, how many grams of Cu deposited?
- 20. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 2.935g of Ni was deposited in the first cell. The amount of Cr deposited in the another cell? Give : molar mass of Nickel and chromium are 58.74 and 52gm⁻¹ respectively.
- 21. A copper electrode is dipped in 0.1M copper sulphate solution at 25°C. Calculate the electrode potential of copper. [Given: $E_{Cu^{2+}|Cu}^{\circ} = 0.34 \text{ V}$].
- 22. For the cell Mg (s) $|Mg^{2+}(aq)|Ag^{+}(aq)|Ag$ (s), calculate the equilibrium constant at 25°C and maximum work that can be obtained during operation of cell. Given : $E^{\circ}_{Mg^{2+}|Mg} = -2.37 V$ and $E^{\circ}_{Ag^{+}|Ag} = 0.80 V$.
- $23.9.2 \times 10^{12}$ litres of water is available in a lake. A power reactor using the electrolysis of water in the lake produces electricity at the rate of 2×10^6 Cs⁻¹ at an appropriate voltage. How many years would at take to completely electrolyse the water in the lake. Assume that there is no loss of water except due to electrolysis.
- 24. Derive an expression for Nernst equation
- 25. Write a note on sacrificial protection.
- 26. Explain the function of H_2 O_2 fuel cell.
- 27. Ionic conductance at infinite dilution of Al^{3+} and SO_4^{2-} are 189 and 160 mho cm² equiv⁻¹. Calculate the equivalent and molar conductance of the electrolyte $Al_2(SO_4)_3$ at infinite dilution.