05

Electrochemistry

Syllabus

5.1 Introduction
5.2 Electric conduction
5.3 Electrical conductance of solution
5.4 Electrochemical cells
5.5 Electrolytic cells
5.6 Galvanic or voltaic cells
5.7 Electrode potential and cell potential
5.8 Thermodynamics of galvanic cells
5.9 Reference electrodes
5.10 Galvanic cells useful in day-to-day life
5.11 Fuel cells
5.12 Electrocehemical series (Electromotive series)

5.1 Introduction

+Q.1 Can you recall?

i. What is a redox reaction?

Ans: A reaction in which oxidation and reduction reaction both occurs simultaneously is called a redox reaction.

ii. Which form of energy is converted into electrical energy in dry cells?

Ans: In dry cells, chemical energy is converted to electrical energy.

iii. How is NaOH manufactured from NaCl?

Ans: NaOH is manufactured by electrolysis of aqueous solution of NaCl.

Q.2 Do you know how does a dry cell generate electricity?

Ans: A chemical reaction occurs in it which generates electricity. Thus in a dry cell chemical energy is converted into electrical energy.

Q.3 How electrical energy is converted into chemical energy through electrolysis.

Ans:

i. Electrolysis is breaking down of an ionic compound by the passage of eletricity.

ii. Breaking down of an electrolyte during electrolysis is a chemical reaction that takes place by the passage of electricity.

iii. Electrical energy is, thus, converted into chemical energy.

Q.4 Define electrochemistry.

Ans:

i. Electrochemistry is the area of chemistry which is concerned with interconversion of chemical and electrical energy.

ii. It also deals with the resistance and conductance of aqueous electrolytic solutions. The determination of conductivities of aqueous electrolytic solutions provide an information on the extent of ionization of electrolytes in water.

Q.5 Give the application of electrochemistry.

Ans:

i. It makes possible the manufacture of essential chemicals. like NaOH, widely used in the manufacture of soaps, detergents and paper, by electrolysis of NaCl.

ii. Electrolysis is possibly the only means to produce fluorine.

iii. The processes such as electro-refining (for purification of metals), electroplating (for coating one metal is on the surface of another) are also electrochemical processes.

Q.6 Where is current electrochemistry research focused on?

Ans: The current research in electrochemistry is focused on the design of fuel cells. The fuel cells are being explored as convenient and compact source of electricity.

Q.7 What are conductors ? What are its different types ?

Ans:

i. A substances through which a charge transfer or flow of electricity can occur are called conductors.

ii. There are two types of conductors which give rise to two types of conduction of electricity. These are
   a. Metallic conductors
   b. Electrolytic or ionic conductors.

+Q.8 Can you recall ?
What is the origin of electical conductivity of metals?

Ans: Metal conduct electricity due to the pressure of free or mobile electrons.

Q.9 Write a short note on : Metallic conduction.

Ans:

i. Electrical condiction through metal involves a direct flow of electrons from one point to the other. This type of conduction is called metallic conduction.

ii. The outermost electrons of metals form conduction bond. The electrons in conduction band are free to move and hence flow under the influence of applied electrical potential.

iii. Metallic conductors are, thus, electronic conductors.

Q.10 Write a note on electrolytic or ionic conduction.

Ans:

i. Electrolytic conduction involves conduction of electric current by the movement of ions of the electrolytes.

ii. In this type of conduction the charge transfer occurs in the form of movement of ions through molten electrolytes or the aqueous solutions of electrolytes.

iii. Substances such as ionic salts, strong or weak acids and bases are the electrolytes.

iv. These dissociate into ions when dissolved in polar solvents such as water. Ionic solids dissociate into ions in molten state as well.

v. Conduction through electrolytic conductors involves transfer of matter from one part of the conductor to the other.

vi. It means that the current flowing through an electrolytic conductor is accompanied by a chemical change.

Q.11 Define non electrolytes.

Ans: A substance that does not readily ionize when dissolved or melted and is a poor conductor of electricity.

Q.12 What are electrolytes? Give its different types.

Ans:

i. The conductivities of their aqueous solutions are higher than that of water. These are called electrolytes. Electrolytes conduct electricity in molten state or when dissolved in water.

ii. On the basis of high or low electrical conductivity electroytes are classified into strong and weak electrolytes.

iii. The substances such as ionic salts, strong acids or bases are almost completely dissociated in aqueous solutions.

iv. These are strong electrolytes. The solutions of strong electrolytes exhibit high conductivities.

v. The weak acids and weak bases are weak electrolyty.

vi. They dissociate to a very small extent in aqueous solutions and show lower conductivity than those of strong electrolytes.

Remember –

Electrolyte is a compound that conducts electricity when molten or in aqueous solution and breaks down into ions during electrolysis.

5.3 Electrical conductance of solution

Q.13 Define resistance and give its S.I. unit.

Ans:

i. According to Ohm's law, the electrical resistance R of a conductor is equal to the electric potential difference V divided by the electric current, I :

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

ii. The SI unit of potential is volt (V) and that of current is ampere (A).

iii. The unit of electrical resistance is ohm denoted by the symbol Ω (omega). Thus, Ω = VA^{-1} .

Note -

The unit of electrical resistance is oh denoted by the symbol Ω (omega) . Thus Ω = VA^{-1}.

Q.14 What is electrical conductance?

Ans:

i. The electrical conductance, G, of a solution is reciprocal of resistance.

$$G = \frac{1}{R}$$

ii. The SI unit of G is siemens, denoted by S, which is equal to Ω^{-1}.

iii. Where C represents coulomb. The unit of electricity related to current strength in ampere and time in seconds as C = As.

Q.15 What is electrical resistance of a conductor?

Ans:

i. The electrical resistance of a conductor is proportional to length l and inversely proportional to cross sectional area a.

$$R \propto \frac{l}{a} \text{ or } R = \rho\frac{l}{a}$$

where ρ, the proportionality constant is called resistivity of the conductor.

ii. Resistivity is the resistance of conductor of unit length and unit cross sectional area.

+Q.16 Can you recall?
What is the S.I. unit of resistivity?

Ans: The S.I unit of resistivity is Ω m.

Q.17 Write a short note on conductivity.

Ans:

i. We know that $G = 1/R$ and R is directly proportional to length and inversely proportional to its cross sectional area.

ii. Therefore, G is directly proportional to a and inversely proportional to the length l. Thus

$$G \propto \frac{a}{l} \text{ or } G = k\frac{a}{l}$$

iii. The proportionality constant k is called conductivity. $G = k$ if length and cross sectional area of conductor are unity.

iv. Thus, conductivity is the electrical conductance of a conductor of unit length and unit area of cross section.

v. In other words, the conductivity is the electrical conductance of unit cube of material.

vi. Conductivity of solution of an electrolyte is called electrolytic conductivity which refers to the electrical conductance of unit volume ($1\ m^3$or $1\ cm^3$) of solution.

vii. The S.I unit of conductivity is Sm^{-1} or Ω^{-1} m^{-1}.

Q.18 Show that conductivity (K) and resistivity (ρ) are inversely proportional.

Ans: We know that

$$k = G\frac{l}{a} = \frac{1}{R}\frac{l}{a} \qquad \text{..................... (i)}$$

$$\text{Now } R = \rho\frac{l}{a} \qquad \text{.................... (ii)}$$

combining eq(i) and (ii) we get

$$k = \frac{1}{P}$$

Note-

Unit of electrolytic conductivity

Q.19 Why molar conductivity is preferred over electrolytic conductivity?

Ans:

i. The electrolytic conductivity is not suitable for comparing conductivities of different solutions.

ii. The conductivity of a solution depends on number of ions present in unit volume of solution.

iii. The solution of higher concentration contains more ions and exhibits higher conductivity than the solution of lower concentration.

iv. To compare conductivities of different solutions, they must have the same concentration.

v. So, we compare the conductivities of 1 mole of different electrolytes in a given volume of solution i.e. molar conductivity.

Q.20 Write a short note on molar conductivity.

Ans:

i. In 1880, the German physicist F.W.G. Kohlrausch introduced the term molar conductivity denoted by $\wedge$ (lambda).

ii. The molar conductivity of an electrolytic solution is the electrolytic conductivity, k, divided by its molar concentration c.

$$\wedge = \frac{k}{c}$$

iii. SI units of k are S m^{-1} and that of c are mol m^{-3}.

iv. Hence SI units of $\wedge$ are S m^2 mol^{-1}.

v. Common units employed for molar conductivity are Ω^{-1} cm^2 mol^{-1}.

★ Q.21 Write the relationship between conductivity and molar conductivity and hence unit of molar conductivity.

Ans:

i. The molar conductivity of an electrolytic solution is the electrolytic conductivity, k, divided by its molar concentration c.

$$\wedge = \frac{k}{c}$$

ii. SI units of k are S m^{-1} and that of c are mol m^{-3}.

iii. Hence SI units of $\wedge$ are S m^2 mol^{-1}.

iv. Common units employed for molar conductivity are Ω^{-1} cm^2 mol^{-1}.

Q.22 Give the significance of molar conductivity ($\wedge$).

Ans:

i. Consider volume of a solution containing 1 mole of dissolved electrolyte. Suppose the solution is placed between two parallel electrodes 1 cm apart and large enough to accommodate it.

ii. The electrical conductance exhibited by this solution is the molar conductivity.

iii. The molar conductivity is the electrical conductance generated by all the ions in 1 mole of the electrolyte.

Remember-

Conductivity is electrical conductance due to all the ions in 1 cm^3 of given solution. Molar conductivity is the electrical conductance due to the ions obtained from 1 mole of an electrolyte in a given volume of solution.

Q.23 Derive a relationship between molar conductivity and electrolytic conductivity.

Ans:

i. Conductivity k is the electrical conductance of 1 cm^3 of solution.

ii. If V is volume of solution in cm^3 containing 1 mole of dissolved electrolyte, its electrical conductance is $\wedge$.

iii. Each 1 cm^3 portion in the volume V has conductance k.

iv. Hence, total conductance of V cm^3 is kV which is molar conductivity.
Thus, we have $\wedge = k\ V$ .... (i)

v. Concentration of solution
$= c$ mol L^{-1}

$$= \frac{c\ \text{mol L}^{-1}}{1000\ \text{cm}^3\ \text{L}^{-1}} = \frac{c}{1000}\text{mol}\,\text{cm}^{-3}$$

vi. Volume, V of solution in cm^3 containing 1 mole of an electrolyte is reciprocal of concentration. Therefore,

$$V = \frac{1}{\text{concentraion}} = \frac{1000}{c}\text{cm}^3\ \text{mol}^{-1} \text{ .... (ii)}$$

vii. Substitution for V in Eq. (i) yields

$$\wedge = \frac{1000k}{c}$$

Q.24 Explain the effect of dilution of solution on conductivity.

Ans:

i. The electrolytic conductivity is electrical conductance of unit volume (1 cm^3) of solution. It depends on the number of current carrying ions present in unit volume of solution.

ii. On dilution total number of ions increase as a result of increased degree of dissociation.

iii. An increase in total number of ions is not in proportion of dilution. Therefore, the number of ions per unit volume of solution decreases. This results in decrease of conductivity with decrease in concentration of solution.

Explanation:

100 cm^3 of solution of an electrolyte contains 8×10^{20} ions. The number of ions per cm^3 is 8×10^{18}.

If the solution is diluted to 1000 cm^3 the total number of ions will increase but not by a factor of 10. Assume that the number of ions increases from 8×10^{20} to 64×10^{20} on dilution. After dilution the number of ions per cm^3 is 6.8×10^{18}.

It is evident that the number of ions per cm^3 decreases from 8×10^{18} to 6.8×10^{18} on dilution from 100 cm^3 to 1000 cm^3 and in turn, the conductivity decreases.

Q.25 Explain the effect of dilution on molar conductivity.

Ans:

i. The molar conductivity is the electrical conductance of 1 mole of an electrolyte in a given volume of solution.

ii. The increasing number of ions produced in solution by 1 mole of the electrolyte lead to increased molar conductivity.

iii. This results in increase in molar conductivity with decrease in concentration of solution.

Q.26 Explain the variation of molar conductivity with concentration in case of strong and weak electrolytes.

Ans:

i. The variation of molar conductivity with concentration in case of strong and weak electrolytes is qualitatively different.

ii. Strong electrolytes :
   a. The molar conductivity of solution of strong electrolyte increases rapidly with dilution.
   b. It approaches the limiting value for 0.001 M or 0.0001 M solution. The dilution has no effect on molar conductivity thereafter. The maximum limiting value of molar conductivity is the molar conductivity at zero concentration or at infinite dilution. It is denoted by $\wedge_0$.
   c. The zero concentration or infinite dilution means the solution is so dilute that further dilution does not increase the molar conductivity.

iii. **Weak electrolytes :**
   a. The molar conductivity of weak electrolytes increases rapidly on dilution.
   b. For concentrations of 0.001M or 0.0001 M, the $\wedge$ value is lower than $\wedge 0$ the molar conductivity at zero concentration.

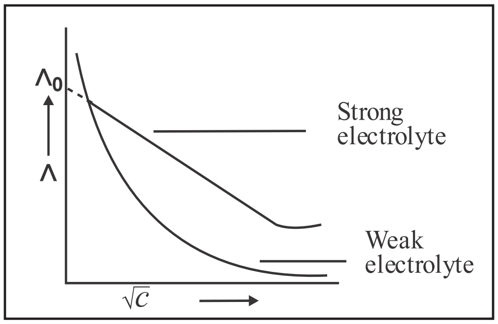
Q.27 How molar conductivity of strong electrolytes can be determined with the help of graphical method ? And why this method cannot be used for weak electrolytes?

Ans:

i. The expression for the molar conductivity of strong electrolyte with concentration is $\wedge = \wedge_0 a\sqrt{c}$ where a is constant and '$\wedge_0$' is molar conductivity at zero concentration or infinite dilution.

ii. The molar conductivity of strong electrolytes varies lenerly with squaure root of concentration

iii. Therefore for a strong electrolytes a plot of $\wedge$ versus $\sqrt{c}$ is linear as shown in the figure.



Variation of Λ with $\sqrt{c}$

iv. The molar conductivity of strong electrolytes at zero concentration can be determined by extrapolation of linear part of '$\wedge$' versus '$\sqrt{c}$'.

v. This method cannot be used for weak electrolytes since $\wedge$ versus $\sqrt{c}$ curve does not approach linearity. Kohlrausch law is useful for calculating $\wedge_0$ of weak electrolytes.

★ Q.28 What is konlraush law of independent migration of ions? How it is useful in obtaining molar conductivity at zero concentration for a weak electrolyte? Explain with an example.

Ans:

i. The law states that at infinite dilution each ion migrates independent of co-ion and contributes to total molar conductivity of an elctrolyte irrespective of the nature of other ion to which it is associated.

ii. Both cation and anion contribute to molar conductivity of the electrolyte at zero concentration and thus $\wedge_0$ is sum of molar conductivity of cation and that of the anion at zero concentration.

iii. Thus, $\wedge_0 = n_+\lambda_+^0 + n_-\lambda_-^0$

iv. where λ_+ and λ_- are molar conductivities of cation and anion, respectively, and n_+ and n_- are the number of moles of cation and anion, specified in the chemical formula of the electrolyte.

v. The theory is particularly useful in calculating $\wedge_0$ values of weak electrolytes from those of strong electrolytes. For example, $\wedge_0$of acetic acid can be calculated by knowing those of HCl, NaCl and CH_3COONa as described below :

$$\wedge_0(HCl) + \wedge_0(CH_3COONa) - \wedge_0(NaCl)$$

$$= \lambda_{H^+}^0 + \lambda_{Cl^-}^0 + \lambda_{CH_3COO^-}^0 + \lambda_{Na^+}^0 - \lambda_{Cl^-}^0$$

$$= \lambda_{H^+}^0 + \lambda_{CH_3COO^-}^0 = \wedge_0(CH_3COOH)$$

Thus,

$$\wedge_0(CH_3COOH) = \wedge_0(HCl) + \wedge_0(CH_3COONa) - \wedge_0(NaCl)$$

vi. Because $\wedge_0$ values of strong electrolytes, HCl, CH_3COONa and NaCl, can be determined by extrapolation method, the $\wedge_0$ of acetic acid can be obtained.

Q.29 Give the applications / uses of Kohlrausch theory.

Ans:

i. The theory can be used to calculate the molar conductivity of an electrolyte at the zero concentration.

ii. For example,

$$\wedge_0(KCl) = \lambda_{K^+}^0 + \lambda_{Cl^-}^0$$

$$\wedge_0[Ba(OH)_2] = \lambda_{Ba^{2+}}^0 + 2\lambda_{OH^-}^0 .$$

iii. Knowing the molar conductivites of ions at infinite dilution, $\wedge_0$values of electrolyte can be obtained.

iv. The theory is particularly useful in calculating $\wedge_0$ values of weak electrolytes from those of strong electrolytes. For example, $\wedge_0$of acetic acid can be calculated by knowing those of HCl, NaCl and CH_3COONa as described below :

$$\wedge_0(HCl) + \wedge_0(CH_3COONa) - \wedge_0(NaCl)$$

$$= \lambda_{H^+}^0 + \lambda_{Cl^-}^0 + \lambda_{CH_3COO^-}^0 + \lambda_{Na^+}^0 - \lambda_{Cl^-}^0$$

$$= \lambda_{H^+}^0 + \lambda_{CH_3COO^-}^0 = \wedge_0(CH_3COOH)$$

Thus,

$$\wedge_0(CH_3COOH) = \wedge_0(HCl) + \wedge_0(CH_3COONa) - \wedge_0(NaCl)$$

v. Because $\wedge_0$ values of strong electrolytes, HCl, CH_3COONa and NaCl, can be determined by extrapolation method, the $\wedge_0$ of acetic acid can be obtained.

Q.30 Give the relationship between molar conductivity and degree of dissociation of weak electrolytes.

Ans:

The degree of dissociation ($\propto$) of weak electrolyte is related to its molar conductivity at a given concentration c by the equation,

$$\propto = \frac{\wedge_c}{\wedge_0} \text{ .... (i)}$$

where $\wedge_c$ is the molar conductivity of weak electrolyte at concentration c ; $\wedge_0$ is molar conductivity at zero concentration.

Try this

+Q.31 Obtain the expression for dissociation constant in terms of using ostwald's dilution law.

Ans:

i. The degree of dissociation ($\propto$) of weak electrolyte is related to its molar conductivity at a given concentration c by the equation,

$$\propto = \frac{\wedge_c}{\wedge_0} \text{ .... (i)}$$

ii. where $\wedge$ c is the molar conductivity of weak electrolyte at concentration c ; $\wedge_0$ is molar conductivity at zero concentration.

iii. According to Ostwald's dilution law, the expression for the dissociation constant (K) of the weak electrolyte can be given as

$$K = \frac{\propto^2 c}{1 - \propto}$$

iv. Substitution the value of $\propto$ from equation (i) into equation (ii)

$$K = \frac{\left(\frac{\wedge_c}{\wedge_0}\right)^2 \times c}{1 - \left(\frac{\wedge_c}{\wedge_0}\right)} = \frac{\left(\wedge_c / \wedge_0\right)^2 c}{\left(\wedge_0 / \wedge_c\right) / \wedge_0}$$

$$= \frac{\left(\wedge_c\right)^2}{\left(\wedge_0\right)^2} \times \frac{c}{\left(\wedge_0 - \wedge_c\right)} \times \wedge_0$$

$$K = \frac{\left(\wedge_c\right)^2}{\left(\wedge_0\right)\left(\wedge_0 - \wedge_c\right)}$$

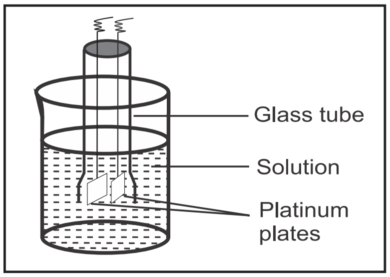
Q.32 Explain conductivity cell with the help of a neat labelled diagram.

Ans:

i. The conductivity cell consists of a glass tube with two platinum plates coated with a thin layer of finely divided platinium black.

ii. This is achieved by the electrolysis of solution of chloroplatinic acid.

iii. The cell is dipped in a solution whose resistance is to be measured as shown in the figure below.



Conductivity cell

Note -

The conductivity of an electrolytic solution is given by $K = \frac{1}{R}\frac{l}{a}$

Q.33 What is a cell constant. What are its units?

Ans:

i. For a given cell, the ratio of separation (l) between the two electrodes divided by the area of cross section (a) of the electrode is called the cell constant.

ii. Thus,

$$\text{Cell constant} = \frac{l}{a} \qquad ....(i)$$

iii. SI unit of cell constant is m^{-1} which is conveniently expressed in cm^{-1}. The Eq. (i) then becomes.

$$k = \frac{\text{cell constant}}{R}$$

Q.34 How is cell constant determined experimentally?

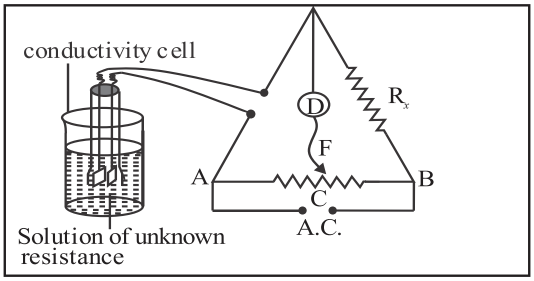
Ans:

i. The cell constant is determined using the 1 M, 0.1 M or 0.01 M KCl solutions.

ii. The conductivity of KCl solution is well tabulated at various temperatures.

iii. The resistance of KCl solution is measured by Wheatstone bridge.

iv. The figure below AB is the uniform wire. R_x is the variable known resistance placed in one arm of Wheatstone bridge.



Measurement of resistance

v. The conductivity cell containing KCl solution of unknown resistance is placed in the other arm of Wheatstone bridge.

vi. D is a current detector. F is the sliding contact that moves along AB. A.C. represents the source of alternating current.

vii. The sliding contact is moved along AB until no current flows. The detector D shows no deflection. The null point is, thus, obtained at C.

viii. According to Wheatstone bridge principle,

$$\frac{R_{solution}}{l(\text{AC})} = \frac{R_x}{l(\text{BC})}$$

Hence, $R_{solution} = \frac{l(\text{AC})}{l(\text{BC})} \times R_x$

ix. By measuring lengths AC and BC and knowing R_x, resistance of KCl solution can be calculated. The cell constant is given by

$$R_{solution} = \frac{l(\text{AC})}{l(\text{BC})} \times R_x$$

Cell constant = $k_{KCl} \times R_{solution}$

x. The conductivity of KCl solution is known. The cell constant, thus, can be calculated.

Q.35 Give and explain the steps through which molar conductivity of an electrolytic solution determined.

Ans:

The determination of molar conductivity of electrolytic solution consist of three steps.

i. a. Determination of cell constant the cell constant is determined by using 1 M, 0.1 M and 0.01 M KCl solution in the conductivity cell.

b. The resistance of KCl solution is determined by wheatstone bridge.

c. Now, cell constant = $k_{KCl} \times R_{solution}$ the conductivity of KCl solution is known. The cell constant thus can be calculated .

ii. **Determination of condictivity of given solution:**

a. KCl solution in the conductivity cell in step (1) is replaced by the given solution whose conductivity is to be measured.

b. Its resistance is measured by the wheatstone bridge.

c. The conductivity of given solution is then calculated as :

$$k = \frac{\text{Cell constant}}{R_{solution}}$$

iii. Calculation of molar conductivity :

a. The molar conductivity of the given solution is then calculated using equation.

b. $\wedge = \dfrac{1000k}{c}$

Type - 1

Numericals based on Molar conductivity

+1. What must be tbe concentration of a solution of silver nitrate to have the molar conductivity of 121.4 Ω^{-1} cm^2 mol^{-1} and the conductivity of 2.428 $\times 10^{-3} \Omega^{-1}$ cm^{-1} at 25°C?

Solution:

Given: Molar conductivity ($\wedge$) of silver nitrate = 121.4Ω^{-1} cm^2 mol,

Conductivity (k) = 2.428× 10^{-3} Ω^{-1} cm^2 mol,

To find: Concentration (c)

Formula : $\wedge = \dfrac{1000k}{c}$

Calculation: Using formula,

$$\wedge = \frac{1000k}{c}$$

$$c = \frac{1000 \times k}{\wedge}$$

$$c = \frac{1000 \times 2.428 \times 10^{-3}}{121.4} = 0.02 \, \text{mol} \, L^{-1} = 0.02M$$

Ans: Concentration of the silver nitrate solution is 0.02 M.

+2. The molar condutivity of 0.05 M $BaCl_2$ solution of 25^0 C is 223 Ω^{-1} cm^2 mol^{-1}. What is its conductivity?

Solution :

$$\wedge = \frac{1000k}{c} \text{ or } k = \frac{\wedge c}{1000}$$

$\wedge$ = 223 Ω^{-1} cm^2 mol^{-1}, c = 0.05 mol L^{-1}

Hence

$$k = \frac{223 \Omega^{-1} \, cm^2 \, mol^{-1} \times 0.05 \, mol \, L^{-1}}{1000 \, cm^3 L^{-1}}$$

= 0.01115 Ω^{-1} cm $^{-1}$

+3. Calculate the molar conductivity of Agl at zero concentration if the molar conduc-tivities at Nal, $AgNO_3$ and $NaNO_3$ at zero concentration are respectively, 126.9, 133.4 and 121.5 Ω^{-1} cm^2 mol^{-1}.

Solution :

According to Kohrausch Law :

i. $\wedge_0$(NaI) = $\lambda^o_{Na+} + \lambda^o_{I-}$

= 126.9 Ω^{-1} cm^2 mol^{-1}

ii. $\wedge_0$($AgNO_3$) = $\lambda^o_{Ag+} + \lambda^o_{NO3-}$

= 133.4 Ω^{-1} cm^2 mol^{-1}

iii. $\wedge_0$($NaNO_3$) = $\lambda^o_{Na+} + + \lambda^o_{NO3-}$

= 121.5 Ω^{-1} cm^2 mol^{-1}

Eq. (i) + eq. (ii) - eq. (iii) gives

$\wedge_0$(NaI) + $\wedge_0$($AgNO_3$) - $\wedge_0$($NaNO_3$)

= $\lambda^o_{Na+} + \lambda^o_{I-} + \lambda^o_{Ag+} + \lambda^o_{NO3-} - \lambda^o_{Ag+} - \lambda^o_{NO3-}$

= $\lambda^o_{Ag+} + \lambda^o_{I-}$

= $\wedge_0$(AgI)

= 126.9 Ω^{-1} cm^2 mol^{-1} + 133.4

$\Omega^{-1}\,cm^2\,mol^{-1} - 121.5\ \Omega^{-1}\,cm^2\,mol^{-1}$

$= 138.8\ \Omega^{-1}\,cm^2\,mol^{-1}$

+4 Try this
Calculate $\wedge_0(CH_2ClCOOH)$ $\wedge_0$if values for HCl, KCl and $CH_2ClCOOK$ are respectively, 4.261, 1.499 and 1.132 $\Omega^{-1}cm^2\ mol^{-1}$.

Solution:

Given : $\wedge_0$ (HCl) = 4.261 cm^2 mol–1

$\wedge_0$ (KCl) = 1.499 cm^2 mol–1

$\wedge_0$ ($CH_2ClCOOK$) = 1.132 cm^{2}mol–1

To find: $\wedge_0$ ($CH_2ClCOOH$)

Formula: $\wedge_0 = \lambda_+^0 + \lambda_-^0$

Calculation: According to Kohlrausch law,

i. $\wedge_0(CH_2ClCOOK) = \lambda^0_{CH_2ClCOO^-} + \lambda^0_{K^+}$

ii. $\wedge_0(HCl) = \lambda^0_{H^+} + \lambda^0_{Cl^-}$

iii. $\wedge_0(KCl) = \lambda^0_{K^+} + \lambda^0_{Cl^-}$

Eq. (i) + Eq. (ii) – Eq. (iii) gives

$= \wedge_0(CH_2ClCOOK) + \wedge_0(HCl) - \wedge_0(KCl)$

$= \lambda^0_{CH_2ClCOO^-} + \lambda^0_{K^+} + \lambda^0_{H^+} - \lambda^0_{K^+} - \lambda^0_{Cl^-}$

$= \lambda^0_{CH_2ClCOO^-} + \lambda^0_{H^+}$

$= \wedge_0$ ($CH_2ClCOOH$)

$= 1.132\ \Omega^{-1}cm^2\ mol^{-1} + 4.261\Omega^{-1}\ cm^2\ mol^{-1}$
$- 1.499\ \Omega^{-1}\ cm^2\ mol^{-1}$
$= 3.894\ \Omega^{-1}cm^2\ mol^{-1}$

Ans: Limiting molar condictivity of $CH_2ClCOOH$, $\wedge_0$ (CH_2ClOOH) is 3.894 $\Omega^{-1}cm^2\ mol^{-1}$.

+5. Calculate molar conductivities at zero concentration for $CaCl_2$ and Na_2SO_4, Given : molar ionic conductivities of Ca^{2+}, Cl^-, Na^+ and SO_4^{2-} ions are respectively, 104, 76.4, 50.1 and 159.6 $\Omega^{-1}\,cm^2\,mol^{-1}$.

Solution :

According to Koharausch Law,

i. $\wedge_0$ ($CaCI_2$) = $\lambda^o{}_{Ca}{}^{2+} + 2\lambda^o{}_{CI-}$

$=104\,\Omega^{-1}\,cm^2\,mol^{-1} + 2\times 76.4\ \Omega^{-1}\,cm^2\,mol^{-1}$

$= 256.8\ \Omega^{-1}\,cm^2\,mol^{-1}$

ii. $\wedge_0$ (Na_2SO_4) = $2\lambda^o{}_{Na+} + \lambda^o{}_{SO4}{}^{2-}$

$= 2\times 50.1\ \Omega^{-1}\,cm^2\,mol^{-1}$

$+ 159.6\ \Omega^{-1}\,cm^2\,mol^{-1}$

$= 259.8\ \Omega^{-1}\,cm^2\,mol^{-1}$.

+6. The molar conductivity of 0.101 M acetic acid at 25^{0}C is 16.5 $\Omega^{-1}\,cm^2\,mol^{-1}$. Calculate its degree of dissociation in 0.01 M solution and dissociation constant if molar conductivity of acetic acid at zero concentration is 390.7 $\Omega^{-1}\,cm^2\,mol^{-1}$.

Solution :

The degree of dissociation,

$$\propto = \frac{\wedge_c}{\wedge_0}$$

$$= \frac{16.6\Omega^{-1}\,cm^2\,mol^{-1}}{390.7\Omega^{-1}\,cm^2\,mol^{-1}} = 0.0422$$

$$K_a = \frac{\propto^2 c}{1-\propto} = \frac{(0.0422)^2\times 0.01}{(1-0.0422)} = 1.85 \times 10^{-5}$$

+7. A conductivity cell containing 0.01 M KCl gives at 25^{0}C the resistance of 604 ohms. The same cell containing 0.001M $AgNO_3$ gives resistance of 6530 ohms. Calculate the molar conductivity of 0.001M $AgNO_3$. [Conductivity of 0.01M KCl at 25^{0}C is 0.00141 $\Omega^{-1}\,cm^{-1}$]

Solution :

i. Calculation of cell constant
Cell constant = $k_{KCl} \times R_{KCl}$
$= 0.00141\ \Omega^{-1}\,cm^{-1} \times 604\ \Omega$
$= 0.852\ cm^{-1}$

ii. Calculation of conductivity of $AgNO_3$

$$k = \frac{\text{Cell constant}}{R} \text{ where } R = 6530\ \Omega$$

$$= \frac{0.852\,cm^{-1}}{6530\,\Omega}$$

$= 1.3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$

iii. Calculation of molar conductivity of $AgNO_3$

$$\wedge = \frac{1000\,k}{c} \qquad \text{Where } c = 0.001\ M$$

$$= \frac{1000\,cm^3\,L^{-1}\times 1.3\times 10^{-4}\,\Omega^{-1}\,cm^{-1}}{0.001\,mol\,L^{-1}}$$

$= 130\ \Omega^{-1}\,cm^2\,mol^{-1}$.

5.4 Electrochemical cells

+Q.36 What is the reaction involving transfer of electrons from one chemical species to another called?

Ans: Redox reactions involve transfer of electrons from one chemical species to another.

Q.37 Write a short note on electrochemical cells.

Ans:

i. An electrochemical cell consists of two metal plates or carbon (graphite) rods. These electronic conductors are dipped into an electrolytic or ionic conductor.

ii. The chemical reaction occuring in electrochemical cells involves transfer of electrons from one species to the other. It is a redox reaction.

iii. Electrochemical reactions, are made of oxidation and reduction half reactions.

iv. The oxidation half reaction occurs at one electrode and the reduction half reaction occurs at the other electrode.

v. The net cell reaction is the sum of these half reactions.

vi. There are two types of electrochemical cells
   a. Electrolytic cell.
   b. Galvanic or voltaic cell.

Q.38 What are electrodes?

Ans:

i. Electrodes are the surfaces on which oxidation and reduction half reactions take place.

ii. Electrodes may or may not participate in the reactions.

Q.39 What are inert electrodes?

Ans: The electrodes which do not take part in reactions are inert electrodes.

Q.42 What are cathode and anode?

Ans:

i. **Cathode :**
   a. It is an electrode at which the reduction takes place.
   b. At this electrode the species undergoing reduction gains electrons.

ii. **Anode :**
   a. It is an electrode at which oxidation takes place.
   b. At this electrode, the species undergoing oxidation loses electrons.

+Q.40 Distinguish between electrolytic and galvanic cells

Ans:

	Electrolytic cell	Galvanic cell
i.	In this type of cell, a nonspontaneous reaction, known as electrolysis, is forced to occur by passing a direct current from an external source into the solution.	In galvanic (voltaic) cell a spontaneous chemical reaction produces electricity.
ii.	In such cells electrical energy is converted into chemcial energy.	In these cells chemical energy is converted into electrical energy.
iii.	The anode of electrolytic cell is positive.	The anode of galvanic cell is negative.
iv.	The cathode of electrolytic cell is negative.	The cathode of galvanic cell is positive.

5.5 Electrolytic cell

Q.41 Write a short note on electrolytic cells.

Ans:

i. Electrolytic cell consists of a container in which electrolyte is placed.

ii. Two electrodes are immersed in the electrolyte and connected to a source of direct current.

iii. At anode (+) a species oxidises with the removal of electrons. These electrons are pulled from anode and pushed to cathode through an external circuit.

iv. The electrons are supplied to species at cathode which are reduced.

Q.42 Explain electrolysis of molten NaCl.

Ans:

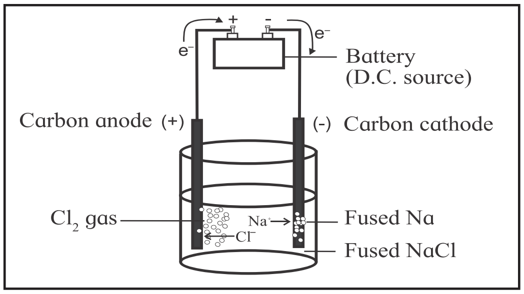
i. Construction of cell :

a. The electrolytic cell consists of a container in which fused NaCl is placed.

b. Two graphite electrodes are immersed in it.

c. They are connected by metallic wires to a source of direct current that is battery. This is shown in the Figure.

d. The carbon electrode connected to terminal electrode of the battery is anode and that connected to negative terminal of the battery is cathode.



Electrolysis of fused NaCl

ii. **Reactions occuring in the cell :**

a. Fused NaCl contains Na^+ and Cl^- ions which are freely mobile.

b. When potential is applied, cathode attracts Na^+ ions and anode attracts Cl^- ions. As these are charged particles, their migration results in an electric current.

c. When these ions reach the respective electrodes, they are discharged according to the following reactions.

iii. **Oxidation half reaction at anode :**

a. Cl ions migrate to anode. Each Cl ion, that reaches anode, gives one electron to anode.

b. It oxidises to neutral Cl atom in the primary process. Two Cl atoms then combine to form chlorine gas in the secondary process.

$$2Cl^-_{(l)} \rightarrow Cl_{(g)} + Cl_{(g)} + 2e^- \quad \text{(priamary process)}$$
$$Cl_{(g)} + Cl_{(g)} \rightarrow Cl_{2(g)} \quad \text{(secondary process)}$$

$$\overline{2Cl^-_{(l)} \rightarrow Cl_{2\,(g)} + 2e^- \quad \text{(overall oxidation)}}$$

c. The battery sucks electrons so produced at the anode and pushes them to cathode through a wire in an external circuit.

b. The battery thus serves as an electron pump.

c. The electrons from the battery enter into solution through cathode and leave the solution through anode.

iv. **Reduction half reaction at cathode :**

a. The electrons supplied by the battery are used in cathodic reduction.

b. Each Na^+ ion, that reaches cathode accepts an electron from the cathode and reduces to metallic sodium.

$$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$$

c. The net cell reaction is the sum of two electrode reactions.

$$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^- \quad \text{(oxidation half reaction)}$$
$$2Na^+_{(l)} + 2e^- \rightarrow 2Na_{(l)} \quad \text{(reduction half reaction)}$$

$$\overline{2Na^+_{(l)} + 2Cl^-_{(l)} \rightarrow 2Na_{(l)} + Cl_{2(g)} \quad \text{(overall cell reaction)}}$$

v. **Results of electrolysis of molten NaCl:**

a. A pale green Cl_2 gas is released at anode.

b. A molten silvery-white sodium is formed at cathode.

c. Decomposition of NaCl into metallic sodium and $Cl_{2(g)}$ is non-spontaneous. The electrical energy supplied by the battery forces the reaction to occur.

Q.43 Write the electrode reaction during electrolysis of molten KCl.

Ans: The electrode reactions during electrolysis of molten KCl can be given as.

$$2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^- \quad \text{(Oxidation half reaction at anode)}$$
$$2K^+_{(l)} + 2e^- \rightarrow 2K_{(l)} \quad \text{(Reduction half reaction at a cathode)}$$

$$\overline{2K^+_{(l)} + 2Cl^-_{(l)} \rightarrow 2K(l) + Cl_{2(g)} \quad \text{(Overall cell reaction)}}$$

Q.44 Explain electrolysis of aqueous NaCl.

Ans:

i. Electrolysis of aqueous NaCl :

a. Electrolysis of an aqueous NaCl can be carried out in the cell used for the electrolysis of molten NaCl using inert electrodes.

b. The fused NaCl is replaced by moderately concentrated aqueous solution of NaCl.

c. The water involved in electrolysis of aqueous NaCl, leads to electrode reactions that differ from electrolysis of molten NaCl.

ii. **Reduction half reaction at cathode :**

a. At cathode, two reduction reactions compete. One is the reduction of Na^+ ions as in case of molten NaCl.

$$Na^+(aq) + e^- \rightarrow Na_{(s)},$$

$$E^o = -2.71\ V \qquad ...(i)$$

b. The other is the reduction of water to hydrogen gas.

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)},$$

$$E^0 = -0.83\ V \qquad ...(ii)$$

c. The standard potential for the reduction of water is higher than that for reduction of Na^+.

d. This implies that water has much greater tendency to get reduced than the Na^+ ion.

e. Hence reaction (ii), that is, reduction of water is the cathode reaction when the aqueous NaCl is electrolysed.

iii. **Oxidation half reaction at anode :**

a. At anode there will be competition between oxidation of Cl ion to Cl_2 gas as in case of molten NaCl and the oxidation of water to O_2 gas.

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-, E^o_{oxi} = -1.36\ V$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 2e^-$$

$$E^o_{oxi} = -0.4\ V$$

b. Standard electrode potential for the oxidation of water is greater than that of Cl ion or water has greater tendency to undergo oxidation.

c. It is, therefore, expected that anode half reaction would be oxidation of water.

d. The experiments have shown, however, that the gas produced at the anode is Cl_2 and not O_2.

e. This suggests that anode reaction is oxidation of Cl to Cl_2 gas.

f. This is because of the overvoltage, discussion of which is beyond the scope of the present book.

vi. **Overall cell reaction:**

It is the sum of electrode reactions.

$$\underset{\text{(oxidation at anode)}}{2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-}$$

$$\underset{\text{(reduction at cathode)}}{2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}}$$

$$\underset{\text{(overall cell reaction)}}{2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2\ OH^-_{(aq)}}$$

iv. **Results of electrolysis of aqueous NaCl**

a. H_2 gas is liberated at cathode.

b. Cl_2 gas is released at anode.

c. Because Na^+ ions remain unreacted and OH ions are formed at cathode, NaCl solution is converted to NaOH solution

Note-

It has been found experimentally that the actual voltage required for electrolysis is greater than that calculated using standard potentials. This additional voltage required is the overpotential.

★ Q.45 Write electrode reaction for the electrolysis of aqueous NaCl.

Ans:

i. Reduction half reaction at cathode :

a. At cathode, two reduction reactions compete. One is the reduction of Na? ions as in case of molten NaCl.

$$Na^+(aq) + e^- \rightarrow Na_{(s)}, E^o = -2.71\ V$$

b. The other is the reduction of water to hydrogen gas.

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)},$$

$$E^0 = -0.83\ V$$

ii. **Oxidation half reaction at anode :**

a. At anode there will be competition between oxidation of Cl ion to Cl_2 gas as in case of molten NaCl and the oxidation of water to O_2 gas.

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-, E^o_{oxi} = -1.36\ V$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 2e^-$$

$$E^o_{oxi} = -0.4\ V$$

iii. **Overall cell reaction:**

It is the sum of electrode reactions.

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \quad \text{(oxidation at anode)}$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \quad \text{(reduction at cathode)}$$

$$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2\,OH^-_{(aq)} \quad \text{(overall cell reaction)}$$

Q.46 How can we calculate the quantity of electricity passed during the electrolysis using reaction stoichiometry?

Ans: To calculate the quantity of electricity (Q) passed during electrolysis, the amount of current, I, passed through the cell is measured. The time for which the current is passed is noted.

$Q(\text{C}) = I(\text{A}) \times t\,(\text{s})$

★**Q.47 How will you calculate the moles of electrons passed and mass of the substance produced during electrolysis of a salt solution using reaction stoichiometry?**

Ans:

i. Calculation of moles of electrons passed

a. Total charge passed is Q (C). The charge of one mole electrons is 96500 coulombs (C). It is referred to as one faraday (F).

b. Hence, Moles of electrons actually passed

$$= \frac{Q(\text{C})}{96500\ (\text{C/mol e}^-)}$$

ii. **Calculation of moles of product formed**

a. The balanced equation for the half reaction occuring at the electrode is devised.

b. The stoichiometry of half reaction indicates the moles of electrons passed and moles of the product formed. For the reaction,

c. $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$, two moles of electrons are required for the production of one mole of Cu.

d. So we can calculate the moles of product formed.

e. The moles of electrons actually passed are given by Q / 96500

f. To simplify further we introduce the entity mole ratio given by

Mole ratio =

$$\frac{\text{moles of product formed in the half reaction}}{\text{moles of electrons required in the half reaction}}$$

For the reaction of Cu, mole ratio = $\frac{1}{2}$

Therefore,

Moles of product formed

= moles of electrons actually passed × mole ratio

$$= \frac{Q(\text{C})}{96500(\text{C/mol e}^-)}$$

iii. **Calculation of mass of product :**

Mass of product

W = moles of product × molar mass of product

$$= \frac{\text{I(A)} \times \text{t(s)}}{96500\ (\text{C/mol e}^-)} \times \text{mole ratio} \times \text{molar mass}$$

$$= \frac{\text{I(A)} \times \text{t(s)}}{96500\ (\text{C/mol e}^-)} \times \text{mole ratio} \times \text{molar mass of product}$$

Q.48 If two cells containing different electrolytes are connected in series. How are the masses of the substances liberated at the electrodes of two cells calculated?

Ans:

i. The mass of the substance produced at the electrode of first cell is given by

$$W_1 = \frac{Q(\text{C})}{96500(\text{C/mol e}^-)} \times (\text{mole ratio})_1 \times \text{M}_1$$

Hence, $\frac{Q(\text{C})}{96500(\text{C/mol e}^-)}$

$$= \frac{W_1}{(\text{mole ratio})_1 \times M_1}$$

ii. Similarly mass of substance liberated at the electrode of second cell is W_2 in the equation,

$$\frac{Q(\text{C})}{96500(\text{C/mol e}^-)} = \frac{W_2}{(\text{mole ratio})_2 \times M_2}$$

iii. M_1 and M_2 are the molar masses of substances produced at the electrodes of cells 1 and 2.

Because $\dfrac{Q(\text{C})}{96500(\text{C / mol e}^-)}$ is the same for both,

We have

$$\frac{W_1}{(\text{mole ratio})_1 \times M_1} = \frac{W_2}{(\text{mole ratio})_2 \times M_2}$$

Type-2

Numericals based on electrolysis

★1. How many electrons would have a total charge of 1 coulomb?

Solution :

Charge on 1e$^-$ is 1.602×10^{-19} coulumb.

$1\ \text{e}^- \equiv 1.602 \times 10^{-19}\ \text{C}$

$\therefore$ Number of electrons having total charge of

$$1\ \text{coulomb} = \frac{1}{1.602 \times 10^{-19}} = 6.242 \times 10^{18}$$

$$\frac{1}{1.602 \times 10^{-19}}$$

$$= \frac{10^{19}}{1.602}$$

$= \text{Antilog}\ [\log 10^{19} - \log 1.602]$
$= \text{Antilog}\ [19 \log 10 - \log 1.602]$
$= \text{Antilog}\ [19 - 0.2046]$
$= \text{Antilog}\ [18.7954]$
$= 6.243 \times 10^{18}$

Ans : The number of electrons having a total charge of 1 coulomb is 6.242×10^{18}.

+2. What is the mass of Cu metal produced at the cathode during the passage of 5 ampere current through $CuSO_4$ solution for 100 minutes. Molar mass of Cu is 63.5 g mol^{-1}.

Solution : i. Stoichiometry for the formation of Cu is $Cu^{2+}\ (aq) + 2e^- = Cu\ (s)$

Hence,

$$\text{mole ratio} = \frac{1\,\text{mol}}{2\,\text{mol e}^-}$$

ii. Mass of Cu formed,

W =

$$\frac{\text{I(A)} \times \text{t(s)}}{96500(\text{C / mol e}^-)} \times \text{mole ratio} \times \text{molar mass of Cu}$$

$$= \frac{5\,\cancel{A} \times 100 \times 60\,\cancel{s}}{96500(\cancel{C} / \cancel{\text{mol}}^{e-})} \times \frac{1\,\cancel{\text{mol}}}{2\,\cancel{\text{mol}}^{e-}}$$

$\times\ 63.5\ \text{g mol}^{-1}$

$= 9.87\ \text{g}$

★3. How many moles of electrons are passed when 0.8 ampere current is passed for 1 hour through molten $CaCl_2$?

Solution :

Given : Current (I) = 0.8 ampere, Time(t) = $1 \times 60 \times 60\,\text{s} = 3600\ \text{s}$

To find : No. of moles of electrons passed through molten $CaCl_2$

Formulae : i. Quantity of electricity passed = I(A) × t(s)

ii. No. of moles of electrons passed =

$$\frac{Q(\text{C})}{96500(\text{C / mol e}^-)}$$

Calculation : Using formula (i),

Quantity of electricity passed = I(A) × t(s)

$= 0.8 \times 3600$

Using formula (ii),

Quantity of electricity passed

$$= \frac{Q(\text{C})}{96500(\text{C / mol e}^-)} =$$

$$\frac{0.8 \times 3600}{96500} = 0.03\,\text{mol e}^-$$

$$\frac{0.8 \times 3600}{96500} = \frac{8 \times 360}{96500}$$

$= \text{Antilog}\ [\ (\log 8 + \log 360) - \log 96500]$
$= \text{Antilog}\ [(0.9031 + 2.5563) - 4.9845]$
$= \text{Antilog}\ [\ 3.4594 - 4.9845]$
$= \text{Antilog}\ [-1.5251]$
$= 0.03\ \text{mol e}^-$

Ans : Number of moles of electrons passed through molten $CaCl_2$ is 0.03 mol e$^-$.

+4. How long will it take to produce 2.415 of Ag metal from its salt solution by passing a current of 3 ampere? Molar mass of Ag is 107.9 g mol^{-1}.

Solution :

i. Stoichiometry :

$Ag^+\ (aq) + e^- \rightarrow Ag\ (s)$

$$\text{mole ratio} = \frac{1\,\text{mole}}{1\,\text{mole e}^-}$$

ii. W =

$$\frac{I(A)\times t(s)}{96500\,(C/mol\,e^-)}\times \text{mole ratio}\times \text{molar mass of Ag}$$

$$2.415\,\cancel{g} = \frac{3\,A\times t}{96500\,(C/\cancel{mol}\,e^-)}\times\frac{1\,\cancel{mol}}{1\,\cancel{mole}\,e^-}$$

$$\times 107.9\,g\,\cancel{mol^{-1}}$$

$$t = \frac{2.415\times 96500\,(C = As)}{3\,A\times 107.9}$$

= 720 s = 12 Min.

★5. What current strength in amperes will be required to produce 2.4 g of Cu from $CuSO_4$ solution in 1 hour? Molar mass of Cu = 63.5 g mol^{-1}.

Solution :

Given :

Mass of Cu = 2.4g,

Molar mass of Cu = 63.5 g mol^{-1}

1 hours = $1\times 60\times 60\,s = 3600\,s$

To find : Current strength (in amperes)

Formulae : i. Molar ratio

$$= \frac{\text{Moles of product formed in half reaction}}{\text{Moles of electrons required in half reaction}}$$

$$\text{ii. } W = \frac{I(A)\times t(s)}{96500\,(C/mol\,e^-)}\times \text{mole ratio}\times \text{molar mass}$$

Calculation : i. Stoichiometry for the formation of Cu is $Cu^{2+}_{(s)} + 2e^- \rightarrow Cu_{(s)}$

Using Formulae (i),

$$\text{Mole ratio} = \frac{1\,mol}{2\,mol\,e^-}$$

ii. Using Formulae (ii),

w =

$$\frac{I(A)\times t(s)}{96500\,(C/mol\,e^-)}\times \text{mole ratio}\times \text{molar mass}$$

$$= 2.4\,g = \frac{I(A)\times t(s)}{96500\,(C/mol\,e^-)}\times\frac{1\,mol}{2\,mol\,e^-}\times 63.5\,g\,mol^{-1}$$

$$I(A) = \frac{2.4\times 96500\times 2}{63.5\times 3600} = 2.03\,A$$

$$= \frac{2.4\times 96500\times 2}{63.5\times 3600}$$

$= \text{Antilog}\,[\,(\log 2.4 + \log 96500 + \log 2) - (\log 63.5 + \log 3600)]$

$= \text{Antilog}\,[\,(\,0.3802 + 4.9845 + 0.3010) - (1.8027 + 3.5563)]$

$= \text{Antilog}\,[\,5.6675 - 5.359] = \text{Antilog}\,(0.3085)$

= 2.034 A

Ans : Current strength in amperes required to produce 2.4 g of Cu from $CuSO_{4.}$

+6. How many moles of electrons are required for reduction of 3 moles of Zn^{2+} to Zn? How many Faradays of electricity will be required?

Solution :

i. The balanced equation for the reduction of Zn^{2+} to Zn is

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

The equation shows that 1 mole of Zn^{2+} is reduced to Zn by 2 moles of electrons. For reduction of 3 moles of Zn^{2+} 6 moles of electrons will be required.

Faraday (96500 Coulombs) is the amount of charge on one mole of electrons.

Therefore, for 6 moles of electrons, 6 F electricity will be required.

+7. In a certain electrolysis experiment 4.36g of Zn are deposited in one cell containing $ZnSO_4$ solution. Calculate the mass of Al deposited in another cell containing $AlCl_3$ solution connected in series with $ZnSO_4$ cell. Molar masses of Zn and Al are 65.4 g mol^{-1} and 27 g mol^{-1}, respectively.

Solution :

Cell 1 :

$Ag^+(aq) + e^- \rightarrow Ag\,(s)$

$$(\text{mole ratio})_1 = \frac{1\,mole}{2\,mole\,e^-}$$

Cell 2 :

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

$$(\text{mole ratio})_2 = \frac{1\,mole}{3\,mole\,e^-}$$

$$\frac{W_1}{(\text{mole ratio}) \times M_1} = \frac{W_2}{(\text{mole ratio})_2 \times M_2}$$

$W_1 = 4.36$ g, $M_1 = 65.4$ g mol^{-1},
$M_2 = 27$ gmol^{-1}
Substitution of the quantities gives

$$\frac{4.36\,\text{g}}{1\cancel{\text{mol}}\text{e} \;/\; 2\cancel{\text{mol}}\text{e}\;\text{e} \times 65.4\,\text{g mol}^{-1}}$$

$$= \frac{W_2}{1\,\cancel{\text{mol}} \;/\; 3\,\cancel{\text{mol}}\text{e} \times 27\,\cancel{\text{g}}\,\cancel{\text{mol}}^{-1}}$$

$$\text{or } \frac{4.36\,\text{g} \times 2}{65.4} = \frac{W_2 \times 3}{27}$$

$$\text{Hence, } W_2 = \frac{4.36\,\text{g} \times 2 \times 27}{65.4 \times 3} = 1.2\text{ g}$$

5.6 Galvanic or voltaic cell

Q.49 Write a short note on galvanic or voltaic cell.

Ans: :

i. In galvanic or voltaic cells, electricity is generated through the use of spontaneous chemical reactions.

ii. A galvanic (or voltaic) cell is made of two half cells. Each half cell consists of a metal strip immersed in the solution of its own ions of known concentration.

iii. Two half cells are constructed by immersing the two metal plates in solutions of their respective ions placed in separate containers.

iv. The two half cells so constructed are combined together to form the galvanic cell.

v. The metal plates called electrodes are connected through voltmeter by a conducting wire for transfer of electrons between them.

vi. To complete the circuit the two solutions are connected by conducting medium through which cations and anions move from one compartment to the other. This requirement is fulfilled by a salt bridge.

Q.50 What is a salt bridge.

Ans: Salt bridge is a U tube containing a saturated solution of an inert electrolyte such as KCl or NH_4NO_3 and 5% agar solution.

Q.51 Write a short note on salt bridge and draw a neat labelled diagram.

Ans:

i. In a galvanic cell, the two solutions are connected by a salt bridge.

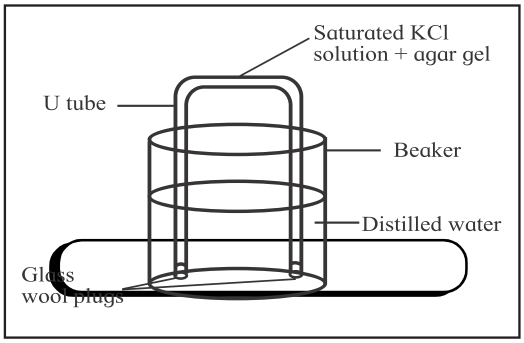
ii. It is an U tube containing a saturated solution of an inert electrolyte such as KCl or NH_4NO_3 and 5 % agar solution.

iii. The ions of electrolyte do not react with the ions of electrode solutions or the electrodes.

iv. Salt bridge is prepared by filling a U tube with hot saturated solution of the salt and agar agar solution allowing it to cool.

v. The cooled solution sets into a gel which does not come out on inverting the tube.

vi. The salt bridge is kept dipped in distilled water when not in use.



Salt bridge

Q.51 What are the functions of salt bridge?

Ans: The salt bridge serves the following functions:

i. It provides an electrical contact between two solutions and thereby completes the electrical circuit.

ii. It prevents mixing of two solutions.

iii. It maintains electrical neutrality in both the solutions by transfer of ions.

Q.52 Write any two functions of salt bridge.

Ans: *Refer Q.51*

Q.53 What are the conventions used to write the cell notation.

Ans:

i. A galvanic cell is represented by a formula or short notation that includes electrodes, aqueous solutions of ions and other species which may or may not be involved in the cell reaction.

ii. The following conventions are used to write the cell notation.

iii. The metal electrodes or the inert electrodes are denoted by vertical lines placed at the ends of the formula or the short notation. The anode (-) is written at the extreme left and cathode (+) at extreme right.

iv. The insoluble species if any or gases are placed in the interior position adjacent to the metal electrodes.

v. The aqueous solutions of ions are placed at the middle of the cell formula.

vi. A single vertical line between two phases indicates the phase boundary. It indicates the direct contact between them.

vii. A double vertical line between two solutions indicates that they are connected by salt bridge.

viii. The additional information such as concentration of solutions and gas pressures is also given.

ix. A single half cell is written in the order: aqueous solution of ions first and then the solid electrode.

★ Q.54 What is the significance of the single vertical line and double vertical line in the formulation galvanic cell?

Ans:

i. A single vertical line between two phases indicates the phase boundary. It indicates the direct contact between them.

ii. A double vertical line between two solutions indicates that they are connected by salt bridge.

+Q55 Salt bridge can be prepared with a laminated long strip of good quality filter paper. Cut the two ends of a laminated strip. Dip the two ends in a saturated solution of KCl for 24 hours. This strip can be used as salt bridge by dipping the two ends in two solutions.

Ans: Notation for anode : $Zn_{(s)}$ | Zn^{2+} (1M)
Notation for cathode: Ca^{2+}(1M) | $Cu_{(s)}$
Cell formula: $Zn_{(s)}$ | Zn^{2+} (1M) || Cu^{2+} (1M) |$Cu_{(s)}$

Q.56 Write the conventions used in writing a cell reaction for a galvanic cell.

Ans:

i. The cell reaction corresponding to the cell notation is an assumption that the right hand side electrode is cathode (+) and left hand side electrode is anode (-).

ii. In galvanic cell oxidation half reaction takes place on the left hand side electrode and reduction half reaction on the right hand side electrode.

iii. The following steps are followed to write the cell reaction.

a Write oxidation half reaction for the left hand side electrode and reduction half reaction for the right hand side electrode.

b. Add two electrode half reactions to get the overall cell reaction. While adding the electrons must be cancelled. For this purpose, it may be necessary to multiply one or both the half reactions by a suitable numerical factor (s). No electrons should appear in the overall reaction.

c. It is important to note that the individual half reactions may be written with one or more electrons. For example, half reactions for H_2 gas, whether written as $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ or $H^+_{(aq)} + e^- \rightarrow 1/2\ H_{2(g)}$ makes no difference. In writing the overall cell reaction, the electrons must be balanced.

Q.57 Write the electrode reactions and overall cell reaction for the cell given below.
$Ni_{(s)}$ |Ni^{2+} (1M)|| Al^{3+} (1M) |$Al_{(s)}$

Ans:

i. Consider the cell,

$$\overset{e^-}{\longrightarrow}$$
$$Ni(s)|Ni^{2+}(1M)||Al^{3+}(1M)|Al(s)$$

The oxidation at anode is

$$Ni_{(s)} \rightarrow Ni^{2+}(1M) + 2e^-$$

ii. The reduction half reaction at cathode is

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

iii. To balance the electrons, oxidation reaction is multiplied by 3 and reduction reaction by 2.

The two half reactions so obtained when added give the overall cell reaction. Thus,

$$\underset{\text{(oxidation half reaction)}}{3\text{Ni(s)} \rightarrow 3\,\text{Ni}^{2+}(1\text{M}) + 6\,e^-}$$
$$\underset{\text{(reduction half reaction)}}{2\,\text{Al}^{3+}(1\text{M}) + 6\,e^- \rightarrow 2\,\text{Al(s)}}$$
$$\underset{\text{(overall cell reaction)}}{\overline{3\,\text{Ni(s)} + 2\text{Al}^{3+}(1\text{M}) \rightarrow 3\text{Ni}^{2+}(1\text{M}) + 2\text{Al(s)}}}$$

Try this

+Q.58 Write electrode reaction and overall cell reaction for Daniel cell you learnt in standard XI.

Ans: Electrode reactions:

The oxidation half reaction at anode is

$$\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}(1\text{M}) + 2e^-$$

The reduction half reaction at cathode is

$$\text{Cu}^{2+}(1\text{M}) + 2e^- \rightarrow \text{Cu}_{(s)}$$

The two half reactions so obtained when added give the overall cell reaction. Thus,

$$\underset{\text{(oxidation half reaction)}}{\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+}(1\text{M}) + 2e^-}$$
$$\underset{\text{(reduction half reaction)}}{\text{Cu}^{2+}(1\text{M}) + 2e^- \rightarrow \text{Cu}_{(s)}}$$
$$\underset{\text{(overall cell reaction)}}{\overline{\text{Zn}_{(s)} + \text{Cu}^{2+}(1\text{M}) \rightarrow \text{Zn}^{2+}(1\text{M}) + \text{Cu}_{(s)}}}$$

Q.59 Formulate a cell from the following electrode reactions:

$$\mathbf{Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}}$$

$$\mathbf{Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-}$$

Ans: The oxidation half reaction at anode is

$$\text{Mg}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2e^-$$

The reduction half reaction at cathode is

$$\text{Au}^{3+}_{(aq)} + 3e^- \rightarrow \text{Au}_{(s)}$$

Natation for anode: $\text{Mg}_{(s)} \mid \text{Mg}^{2+}{}_{(aq)}$
Notation for cathode: $\text{Au}^{3+}{}_{(aq)} \mid \text{Au}_{(s)}$
Cell formula:
$\text{Mg}_{(s)} \mid \text{Mg}^{2+}{}_{(aq)} \parallel \text{Au}^{3+}{}_{(aq)} \mid \text{Au}_{(s)}$

5.7 Electrode potential and cell potential

Q.60 Write a short note on electrode potential.

Ans:

i. A galvanic cell is composed of two half cells, each consisting of electronic (metal plates) and electrolytic (solution of ions) conductors in contact.

ii. At the surface of separation of solid metal and the solution, there exists difference of electrical potential.

iii. This potential difference established due to electrode half reaction occurring at the electrode surface, is the electrode potential.

Q.61 Define the following terms.
i. Oxidation potential
ii. Reduction potential

Ans:

i. Oxidation potential : The potential associated with oxidation reaction is called oxidation potential.

ii. **Reduction potential :** The potential associated with reduction reaction is called reduction potential.

Q.62 What is electromotive force or cell potential?

Ans:

i. The overall cell potential, also called electromotive force (emf), is made of the contributions from each of the electrodes.

ii. In other words, the cell potential is algebraic sum of the electrode potentials,
$E_{cell} = E_{oxi}$ (anode) + E_{red} (cathode)

iii. where E_{oxi} is the oxidation potential of anode (-) and E_{red} is the reduction potential of cathode (+).

Note-

When galvanic cell operates, electrons are generated at the anode. These electrons move through external circuit to the cathode. The cell potential is the force that pushes electrons away from anode (-) and pulls them toward cathode where they are consumed.

Q.63 Why it is necessary to measure the cell voltage under given set of standard conditions of concentration and temperature.

Ans:

i. The electrode potential and the cell potential depend on concentrations of solutions, pressures of gases and the temperature.

ii. To facitilate comparison of different galvanic cells, it is necessary to measure the cell voltage under given set of standard conditions of concentration and temperature.

Q.64 Write a short note on electrode potential.

Ans:

i. The standard conditions chosen are 1M concentration of solution, 1 atm pressure for gases, solids and liquids in pure form and 25^0C.

ii. The voltage measured under these conditions is called standard potential designated as E^0.

iii. The standard cell potential is the algebraic sum of the standard electrode potentials.

$E^0_{cell} = E^0_{oxi}$ (anode) + E^0_{red} (cathode)

iv. Here $E0_{oxi}$ is standard oxidation potential and $E0_{red}$ is the standard reduction potential.

v. It follows that the standard cell potential (emf) is written in terms of the standard potentials of the electrodes.

$E^0_{cell} = - E^0_{red}$ (anode) + E^0_{red} (cathode)

vi. Omitting the subscript red, we have

$E^0_{cell} = E^0$ (cathode, +) – E^0(anode, –)

Note-

It must be realised that standard oxidation potential of any electrode is numerically equal to its standard reduction potential with the reversal of sign. For example standard oxidation potential of Zn^{2+} (1M) | Zn electrode is 0.76V. Its standard reduction potential will be – 0.76 V. Hereafter the standard reduction potential will be called standard potential, the voltage associated with a reduction reaction.

Remember-

i. While constructing a galvanic cell from two electrodes, the electrode with higher standard potential is cathode (+) and that with lower standard potential is anode (-).

ii. The difference in electrical potential between anode and cathode is cell voltage.

Q.65 Under what conditions the cell potential is called standard cell potential.

Ans:

i. The standard condition chosen are 1 M concentration of solution, 1 atm pressure for gases, solids and liquids in pure form and 25 ºC.

ii. The voltage measured under these conditions is called standard potential.

Q.66 Write Nernst equation. What part of it represents the correction factor for non-standard state conditions?

Ans:

i. Dependence of cell voltage on concentrations is given by Nernst equation. For any general reaction,

$$aA + bB \rightarrow cC + dD$$

ii. The cell voltage is given by

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \text{In} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$= E^0_{Cell} - \frac{2.303RT}{nF} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where n = moles of electrons used in the reaction, F = Faraday = 96500 C, T = temperature in kelvin, R = gas constant = 8.314 J $K^{-1}mol^{-1}$

At $25°C, \frac{2.303RT}{F} = 0.0592V$

iii. Therefore at 25 ^{0}C, eq. (i) becomes

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{n} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q.67 What does the first term on the right hand side of nerst requation represent?

Ans: The first term on the right hand of Nernst equation represents standard state electrochemical conditions.

Note-

The cell potential equals standard potential if the concentrations of reactants and products are 1 M each. Thus,
if [A] = [B] = [C] = [D] = 1M,
$E_{cell} = E^0_{cell}$
If a gaseous substance is present in the cell reaction its concentration term is replaced by the partial pressure of the gas.

Q.68 Give the application of Nerst equation.

Ans:

i. The Nernst equation can be used to calculate cell potential and electrode potential.

ii. **Calculation of cell potential :**

a. Consider the cell

$Cd(s)\ |Cd^{2+}(aq)\ ||Cu^{2+}\ (aq)\ |\ Cu.$

Let us first write the cell reaction

$$Cd_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2e^- \quad \text{oxidation at anode)}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad \text{(reduction at cathode)}$$

$$Cd_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cd^{2+}_{(aq)} + Cu_{(s)} \quad \text{(overall cell reaction)}$$

Here $n = 2$

b. The potential of cell is given by Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.0592}{2}\log_{10}\frac{\left[Cd^{2+}\right]}{\left[Cu^{2+}\right]}$$

at 25 °C

(Concentration of solids and pure liquids are taken to be unity.)

Type-3

Numericals based on standard electrode potential and nerst equation

★1. **What is standard cell potential for the reaction $3Ni_{(s)}$ + $2Al^{3+}$ (1 M) → $3Ni^{2+}$ (1 M) + $2Al_{(s)}$, if E^0_{Ni} = – 0.25 V and E^0_{Al} = –1.66 V?**

Solution :

Given : E^0_{Ni} = – 0.25 V, E^0_{Al} = –1.66 V

To find : Standard cell potential

Formulae : $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

Calculation : Electrode reactions are

At anode : $Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e-$

At canode : $Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$

The standard electrode potential is given by

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$E^0_{cell} = E^0_{Al} - E^0_{Ni} = (-1.66\ V) - (-0.25\ V)$

$= -1.41\ V$

Ans : The standard cell potential for the reaction is – 1.41 V.

★2. **Construct a galvanic cell from the electrodes Co^{3+} | Co and Mn^{2+} | Mn. E^0_{Co} = 1.82 V, E^0_{Mn} = -1.18 V. Calculate E^0_{cell}.**

Solution :

Given : E^0_{Co} = 1.82 V

E^0_{Mn} = -1.18 V

To find : E^0_{cell} and cell representation

Formulae : $E^0_{cell} = E^0_{Cathode} - E^0_{anode}$

Calculation : Electrode reactions are

At anode : $3(Mn_{(s)} \rightarrow Mn^{2+}_{(aq)} + 2e^-)$

At cathode : $2(Co^{3+}_{(aq)} + 3e^- \rightarrow Co_{(s)})$

The cell is composed of Mn (anode), $Mn_{(S)}\,|Mn^{2+}_{(aq)}$ and Co (cathode), $Co^{3+}_{(aq)}\,|Co_{(s)}$.

The cell is represented as: $Mn_{(s)}\,|\,Mn^{2+}_{(aq)}\,||Co^{3+}_{(aq)}\,|\,Co_{(s)}$

The standard electrode potential is given by

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{Co} - E^0_{Mn}$$
$$= 1.82V - (-1.18V) = 3.00V$$

Ans: The dtandard cell potential is 3.00 V.

+3. **Calculate the voltage of the cell. Sn (s) | Sn^{2+} (0.02M) | Ag^+ (0.01M) | Ag (s) at 25 ^{0}C. E^0_{Sn} = – 0.136 V, E^0_{Ag} = 0.800 V.**

Soultion : First we write the cell reaction.

$Sn \rightarrow (s)\ Sn^{2+}\ (0.02M) + 2\ e^-$ (oxidation at anode)

$[\ Ag^+\ (0.01M) + e^- \rightarrow Ag\ (s)\ ]$ (reduction at cathode)

$Sn\,(s) + 2\,Ag^+\,(0.01M) \rightarrow$

$Sn^{2+}\ (0.02\ M) + 2\ Ag\ (s)$ (overall cell reaction)

The cell potential is given by

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{2}\log_{10}\frac{[Sn^{2+}]}{[Ag^+]^2}$$

$$E_{cell} = E^0_{Ag} - E^0_{Sn} = 0.8\ V + 0.136\ V$$

$$= 0.936\ V$$

Hence,

$$E_{cell} = 0.936V - \frac{0.0592V}{2}\log_{10}\frac{0.02}{(0.01)^2}$$

$$= 0.936V - \frac{0.0592V}{2}\log_{10}200$$

$$= 0.936V - \frac{0.0592V}{2}\times 2.301$$

$$= 0.936V - 0.0681V = 0.8679\ V$$

★4. **Calculate emf of the cell at 25 °C. $Zn_{(s)}$ | Zn^{2+}(0.08 M) || Cr^{3+} (0.1 M) | $Cr_{(s)}$ E^o_{zn} = – 0.76 V, E^o_{cr} = – 0.74 V**

Solution:

Given : $E^0_{zn} = -0.76V,\ E^0_{Cr} = -0.74V$

To find: Emf of the cell (E_{cell})

Formulae:

i. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

ii. $E_{cell} = E^0_{cell} - \frac{0.0592\,V}{n}\log_{10}\frac{[Product]}{[Reactant]}$

Calculation: Cell reaction

$$[Zn_{(s)} \rightarrow Zn^{2+}_{(0.08M)} \underset{\text{(oxidation at anode)}}{+2e^-}]\times 3$$

$$[Cr^{3+}_{(0.1M)} + 3e^- \rightarrow \underset{\text{(reduction at cathode)}}{Cr_{(s)}}]\times 2$$

$$\overline{3Zn_{(s)} + 2Cr^{3+}_{(0.1M)} \rightarrow \underset{\text{(overall reaction)}}{3\,Zn^{2+}_{(0.08M)}} + 2Cr_{(s)}}$$

Using formula (i),

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Cr} - E^0_{Zn} = -0.74\,V - (-0.76V) = 0.02V$$

Using formula (ii),

The cell potential is given by

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{n}\log_{10}\frac{[Product]}{[Reactant]}$$

$$= 0.02 - \frac{0.0592V}{6}\log_{10}\frac{(0.08)^3}{(0.1)^2}$$

$$= 0.02 + 0.0127 = 0.0327\ V$$

Ans: The emf of the cell is 0.0327V.

★5. **Calculate emf of the cell: $Zn_{(s)}|Zn^{2+}(0.2\ M)||$ H^+ (1.6 M) | H_2(g, 1.8 atm) | Pt at 25 ºC.**

Solution:

Given: $[Zn^{2+}] = 0.2$ M, $[H^+] = 1.6$, $P_{H_2} = 1.8\,atm$

To find: Emf of the cell (Ecell)

Formulae:

i. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

ii. $E_{cell} = E^0_{cell} - \frac{0.0592\,V}{n}\log_{10}\frac{[Product]}{[Reactant]}$

Calculation: cell reaction

$$Zn_{(s)} \rightarrow \underset{\text{oxidation at anode}}{Zn^{2+}_{(0.2M)}} + 2e^-$$

$$2H^+_{(1.6)}\,2e^- \rightarrow \underset{\text{reduction at cathode)}}{H_{2(1.8\,atm)}}$$

$$\overline{Zn_{(s)} + 2H^+_{(1.6M)} \rightarrow \underset{\text{(overall reaction)}}{Zn^{2+}_{(0.2M)}} + H_{2(1.8atm)}}$$

$E^0_{H_2} = 0.0V$ and $E^0_{Zn} = -0.763V$

Using formula (i),

$$E^0_{Cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{H_2} - E^0_{Zn} = 0.0\,V - (-0.763V) = 0.763V$$

Using formula (ii),

The cell potential is given by

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{2}\log_{10}\frac{[Product]}{[Reactant]}$$

$$= 0.763 - \frac{0.0592V}{2}\log_{10}\frac{(0.2)(1.8)}{(1.6)^2}$$

$$= 0.763 + 0.0252 = 0.787\ V$$

Ans: The emf of the cell is 0.7882 V.

+6. The standard potential of the electrode, Zn^{2+} (0.02 M) | Zn (s) is -0.76 V. Calculate its potential.

Solution : Electrode reaction :

Zn^{2+} (0.02M) + 2 e^- → Zn (s)

$$E_{Zn} = E^0{}_{Zn} - \frac{0.0592V}{n}\ \log_{10}\frac{1}{[Zn^{2+}]}$$

$$= -\ 0.76\ V + \frac{00592V}{2}\log_{10}(0.02)$$

$$= -\ 0.76\ V + \frac{00592V}{2}\times(-1.6990)$$

$$= -\ 0.76\ V - 0.0503V = -\ 0.81\ V$$

5.8 Thermodynamics of galvanic cells

Q.69 Derive the relation between Gibbs energy of cell reactions and cell potential.

Ans: :

i. The electrical work done in a galvanic cell is the electricity (charge) passed multiplied by the cell potential.

ii. Electrical work = amount of charge passed × cell potential.

iii. Charge of one mole electrons is F coulombs.

iv. For the cell reaction involving n moles of electrons.
charge passed = *nF* coulombs
Hence, electrical work = nFE_{cell}

v. W. Gibbs in 1878 concluded that electrical work done in galvanic cell is equal to the decrease in Gibbs energy, – Δ*G*, of cell reaction.

vi. It then follows that

Electrical work = - ΔG

and thus - $\Delta G = nFEcell$

or $\Delta G = -nFE_{cell}$

★ Q.70 Using the relationship ΔG^o of cell reaction and the standard potential associated with it, how will you show that the electrical potential is an intersive property.

Ans:

i. Under standard state conditions, we write $\Delta G^0 = -nFE^0_{cell}$ .... (i)

ii. The Eq. (i) explains why E^0_{cell} is an intensive property.

iii. ΔG^0 is an extensive property since its value depends on the amount of substance.

iv. If the stoichiometric equation of redox reaction is multiplied by 2 that is the amounts of substances oxidised and reduced are doubled, ΔG^0 doubles.

v. The moles of electrons transferred also doubles. The ratio,

$$E^0_{cell} = -\frac{\Delta G^0}{nF} \text{ then becomes}$$

$$E^0_{cell} = -\frac{2\Delta G^0}{2nF} = -\frac{\Delta G^0}{nF}$$

vi. Thus, E^0_{cell} remains the same by multiplying the redox reaction by 2. It means E^0_{cell} is independent of the amount of substance and the intensive property.

Remember-

For chemical reaction to be spontaneous, ΔG must be negative. Because $\Delta G = -nFE_{cell}$, E_{cell} must be positive for a cell reaction if it is spontaneous.

★ Q.71 Derive the relationship between standard cell potential and equilibrium constant of cell reaction.

Ans:

i. The relation between standard Gibbs energy change of cell reaction and standard cell potential is given by.

$-\Delta G^0 = nFE^0_{cell}$ .... (i)

ii. The relation between standard Gibbs energy change of a chemical reaction and its equilibrium constant as given in thermodynamics is :

$\Delta G^0 = -RT \ln K$ .... (ii)

iii. Combining Eq. (i) and Eq. (ii), we have

$$-nFE^0_{cell} = -RT \ln K$$

$$\text{or} \quad E^0_{cell} = \frac{RT}{nF} \text{In } K$$

$$= \frac{2.303\ RT}{nF} \log_{10} K$$

$$= \frac{0.0592}{n} \log_{10} K \quad \text{at } 25\ ^oC$$

Try this

Q.72 Write expressions to calculate equilibrium constant from

i. Concentration data

ii. Thermochemical data

iii. Electrochemical data

Ans:

i. **Concentration data:**

For a general reaction, $aA + bB \rightarrow cC + dD$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

ii. **Thermochemical data:**

$\Delta G^o = -RT \text{ In } K$

iii. **Electrochemical data:**

$$E^0_{cell} = \frac{0.0592}{n} \log_{10} K \ \ (\text{at } 25\ ^oC)$$

Type 4

Numericals based on standard Gibbs free energy and standard potential of cell

+1. Calculate standard Gibbs energy change and equilibrium constant at 25^0 C for the cell reaction.

$Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$

Given :

$E^0_{Sn} = -0.136$ V. Write formula of the cell.

Solution :

i. The cell is made of two electrodes, Cd^{2+} (aq) | Cd (s) and Sn_{2+} (aq) | Sn (s). E^0 value for Sn^{2+} (aq) | Sn (s) electode is higher than that of Cd^{2+} (aq) | Cd (s) electrode. Hence, Sn^{2+} (aq) | Sn (s) electrode is cathode and Cd^{2+} (aq) | Cd (s) anode. Cell formula is Cd (s) | Cd^{2+} (aq) | | Sn^{2+} (aq) | Sn (s)

ii. $\Delta G^0 = -nF E^0_{cell}$

$E^0_{cell} = E^0_{Sn} - E^0_{Cd} = -0.136\ V - (-0.403V)$

$= 0.267$ V.

$n = 2$ mol e^-

$$\Delta G^{0} = -2\ \cancel{\text{mol}}\,e^{-}\,96500\ \text{C}/\cancel{\text{mol}}\,e^{-} \times 0.267\ \text{V}$$

$= -51531\ \text{V C} = -51531\ \text{J} = -51.53\ \text{kJ}$

iii. $E^{0}_{cell} = \dfrac{0.0592\ \text{V}}{2}\log_{10}K$

$$0.267\ \cancel{\text{V}} = \frac{0.0592\ \cancel{\text{V}}}{2}\log_{10}K$$

$$\log_{10}K = \frac{0.0267\times 2}{2} = 9.0203$$

$K = \text{antilog}\ 9.0203 = 1.05\times 10^{9}$

★2. Equilibrium constant of the reaction, $2Cu^{+}_{(aq)} \rightarrow \mathbf{Cu^{2+}_{(aq)}} + \mathbf{Cu_{(s)}}$ is . 1.2 × 10^{6} What is the standard potential of the cell in which the reaction takes place?

Solution :

Given: Equilibrium constant of the reaction (K) = 1.2×10^{6}

To find : Standard potential of cell (E^{0}_{cell})

Formulae : $E^{0}_{cell} = \dfrac{0.0592\ \text{V}}{n}\log_{10}K$

Calculation : For the given reaction, n = 1

Using Formula,

$$E^{0}_{cell} = \frac{0.0592}{1}\log_{10}(1.2\times 10^{6})$$

$= 0.0592 \log_{10}(1.2\times 10^{6})$

$= 0.0592 \times (\log_{10} 1.2 + \log_{10} 10^{6})$

$= 0.0592 \times (0.0791 + 6 \log_{10} 10)$

$= 0.0592 \times 6.0791$

$= \text{Antilog}\ (\log 0.0592 + \log 6.0791)$

$= \text{Antilog}\ (-1.2276 + 0.7838)$

$= \text{Antilog}\ (-0.4438)$

$= 0.3599\text{V}$

$E^{0}_{cell} = 0.0592\times(6.079) = 0.36\ \text{V}$

Ans : The standard cell potential of cell is 0.36 V.

5.9 Reference electrode

Q.73 It is impossible to measure the potential of a single electrode. Comment.

Ans:

i. Every oxidation needs to be accompanied by reduction. The occurrence of only oxidation or only reduction is not possible.

ii. In a galvanic cell oxidation and reduction occur simultaneously.

iii. The potential associated with the redox reaction can be experimentally measured.

iv. For the measurement of potential two electrodes need to be combined together where the redox reaction occurs.

+Q.74 What would happen it potential of one of the electrode in the galvanic cell?

Ans:

i. There are two electrodes combined together and a redox reaction results. The measured cell potential is algebraic sum of two electrode potentials.

ii. One electrode potential is zero. Therefore, the measured cell potential is equal to the potential of other electrode.

Q.75 Which electrode is chosen by chemist as a primary reference electrode?

Ans:

i. The chemists have chosen hydrogen gas electrode consisting of H_2 gas at 1 atm pressure in contact with 1 M H^{+} ion solution as a primary reference electrode.

ii. The potential of this electrode has arbitrarily been taken as zero. The electrode is called standard hydrogen electrode (SHE).

Q.76 Give some examples of primary reference electrode.

Ans: Several other electrodes namely calomel, silver-silver chloride and glass electrodes with known potentials are used as secondary reference electrodes.

Note-

The potentials of these electrodes are determined using SHE.

Q.77 Define reference electrode

Ans: A reference electrode is then defined as an electrode whose potential is arbitrarily taken as zero or is exactly known.

Q.78 Describe the operation of standard hydrogen electrode and draw a neat labelled diagram.

Ans:

i. SHE consists of a platinum plate, coated with platinum black used as electrodes.

ii. This plate is connected to the external circuit through sealed narrow glass tube containing mercury.

iii. It is surrounded by an outer jacket.

iv. The platinum electrode is immersed in 1 M H^{+} ion solution.

v. The solution is kept saturated with dissolved H_2 by bubbling hydrogen gas under 1 atm pressure through the side tube of the jacket as shown in the figure.

vi. Platinum does not take part in the electrode reaction. It is inert electrode and serves as the site for electron transfer.

vii. Formulation : Standard hydrogen electrode is represented as

H^+ (1M) | H_2(g, 1atm) | Pt

viii. Electrode reaction : The platinum black capable of adsorbing large quantities of H_2 gas, allows the change from gaseous to ionic form and the reverse process to occur.

ix. The reduction half reaction at the electrode is

$$2H^+(1M) + 2e^- \rightarrow H_2(g, atm)$$

$$E^0_{H_2} = 0.000\,V$$

Q.79 Give the application of SHE (Standard) hydrogen electrode.

Ans:

i. SHE is used as a primary reference electrode to determine the standard potentials of other electrodes.

ii. To determine the standard potential of Zn^{2+}(1M)|Zn $_{(s)}$, it is combined with SHE to form the cell,

Zn|Zn^{2+}(1M)||H^+ (1M)|H_2 (g, 1atm)|Pt

iii. The standard cell potential, E^0_{cell}, is measured.

$E^0_{cell} = E^0_{H_2} - E^0_{zn}, = -E^0_{zn}$ because $E^0_{H_2}$ is zero.

iv. Thus, the measured emf of the cell is equal to standard potential of Zn^{2+}(1M)|Zn $_{(s)}$ electrode.

Q.80 Enlist the difficulties in setting standard hydrogen electrode.

Ans:

i. It is difficult to obtain pure and dry hydrogen gas.

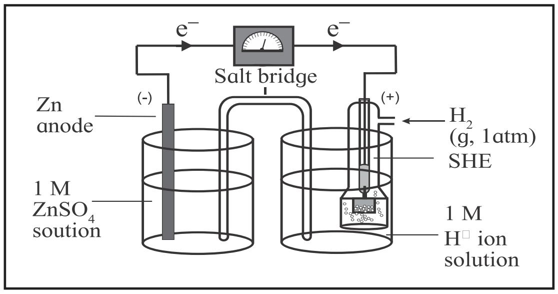
ii. The pressure of hydrogen gas cannot be maintained exactly at 1 atm throughout the measurement.

iii. The concentration of H^+ ion solution cannot be exactly maintained at 1 M. Due to bubbling of gas into the solution, evaporation of water may take place. This results in changing the concentration of solution.

Q.81 Consturct a labelled diagram for the following cell.
Zn|Zn^{2+}(1M)||H^+(1M)|H_2(g, 1 atm) | Pt

Ans: In the given representation of the cell, a standard Zn2+ (1 M) | Zn electrode is combined with standard hydrogen electrode to form the cell.

Zn|Zn^{2+}(1M)||H^+(1M)|H_2(g, 1 atm) | Pt



Determination of standard potential using SHE

Q.82 Derive the expression to calculate standard electrode potential for hydrogen gas electrode.

Ans:

i. For hydrogen gaselectrode,

$H^+(aq) \,|\, H_2(g, P_{H_2}) \,|\, Pt, \left[H^+\right]$ and pressure of hydrogen gas differ from unity.

ii. Electrode reaction:

$$2H^+(aq) + 2e^- \rightarrow H_2(g, P_{H_2})$$

iii. From the Nernst equation

$$E_{H_2} = E^0_{H_2} - \frac{0.0592}{2}\log_{10}\frac{P_{H_2}}{\left[H^+\right]^2}$$

$$= -\frac{0.0592}{2}\log_{10}\frac{P_{H_2}}{\left[H^+\right]^2}$$

Because $E^0_{H_2} = 0$

5.10 Galvanic cells useful in day to day life

Q.83 Write a short note on
i. Primary voltaic cells
ii. Secondary voltaic cells.

Ans: Voltaic (or galvanic) cells in common use can be classified as primary and secondary cells.

i. Primary voltaic cells :

a. When a galvanic cell discharges during current generation, the chemicals are consumed.

b. In primary voltaic cell, once the chemicals are completely consumed, cell reaction stops.

c. The cell reaction cannot be reversed even after reversing the direction of current flow or these cells cannot be recharged.

d. The most familiar example is dry cell.

ii. Secondary voltaic cells :

i. In secondary voltaic cell, the chemicals consumed during current generation can be regenerated.

b. For this purpose an external potential slightly greater than the cell potential is applied across the electrodes.

c. This results in reversal of the direction of current flow causing the reversal of cell reaction. This is recharging of cell.

d. The voltaic cells which can be recharged are called secondary voltaic cells.

Q.84 Which type of cells acts as both galvanic and electrolytic cells? Give examples.

Ans: Secondary cells are galvanic cells during discharge and electrolytic cells during recharging. Examples of secondary cells are lead storage battery, mercury cell and nickel-cadmium cell.

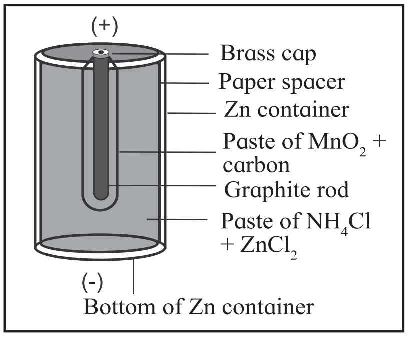
Q.85 Expain the construction and cell reaction of Dry cell

Ans: **Dry cell (Leclanche' cell) :** It is a cell without liquid component, but the electrolyte is not completely dry. It is a viscous aqueous paste.

Construction : The container of the cell is made of zinc which serves as anode (-). It is lined from inside with a porous paper to separate it from the other material of the cell. An inert graphite rod in the centre of the cell immersed in the electrolyte paste serves as cathode. It is surrounded by a paste of manganese dioxide (MnO_2) and carbon black. The rest of the cell is filled with an electrolyte. It is a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). Some starch is added to the paste to make it thick so that it cannot be leaked out.

The cell is sealed at the top to preventdrying of the paste by evaporation of moisture.

See Fig.



Dry cell (leclanche' cell)

Cell reactions:

i. Oxidation at anode :

When the cell operates the current is drawn from the cell and metallic zinc is oxidised to zinc ions.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

ii. Reduction at cathode :

The electrons liberated in oxidation at anode flow along the container and migrate to cathode. At cathode NH_4^+ ions are reduced.

$$2NH^+_{4(aq)} + 2e^- \longrightarrow 2NH_{3(aq)} + H_{2(g)}$$

Hydrogen gas produced in reduction reaction is oxidised by MnO_2 and prevents its collection on cathode.

$$H_{2(g)} + 2MnO_{2(s)} \longrightarrow Mn_2O_{3(s)} + H_2O_{(l)}$$

The net reduction reaction at cathode is combination of these two reactions.

$$2NH_{4(aq)}^{+} + 2MnO_{2(s)} + 2e^{-} \longrightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$$

iii. Net cell reaction :

The net cell reaction is sum of oxidation at anode and reduction at cathode.

$$Zn_{(s)} + 2NH_{4(aq)}^{+} + 2MnO_{2(s)} \longrightarrow Zn_{(s)}^{2+} + Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$$

The ammonia produced combines with Zn^{2+} to form soluble compound containing complex ion.

$$Zn_{(aq)}^{2+} + 4NH_{3(aq)} \longrightarrow [Zn(NH_3)_4]_{(aq)}^{2+}$$

★ Q.86 What are a node and cathode for leclanche dry cell? Write electrode reactions and overall cell reaction when it generates electricity.

Ans: The container of the cell is made of zinc which serves as anode (–). It is lined from inside with a porous paper to separate it from the other material of the cell.

a. Oxidation at anode: $Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}$

b. Reduction at cathode : $2NH_{4(aq)}^{+} + 2MnO_{2(s)} + 2e^{-} \longrightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$

c. Net cell reaction : $Zn_{(s)} + 2NH_{4(aq)}^{+} + 2MnO_{2(s)} \longrightarrow Zn_{(s)}^{2+} + Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$

Do you know ?

Alkaline dry cell : The Leclanche' dry cell works under acidic conditions due to the presence of NH_4Cl. The difficulty with this dry cell is that Zn anode corrodes due to its actions with H^+ ions from NH_4^+ ions.

This results in shortening the life of dry cell. To avoid this a modified or of the dry cell called alkaline dry cell has been proposed. In alkaline dry cell NaOH or KOH is used as electrolyte in place of NH_4Cl. The alkaline dry cell has longer life than acidic dry cell since the Zn corrodes more slowly.

Q.87 What are the uses of dry cell?

Ans: Dry cell is used as a source of power in flashlights, portable radios, tape recorders, clocks and so forth.

Q.88 Give the construction cell reaction during discharge and recharge of lead storage battery

Ans: Lead accumulator stores electrical energy due to regeneration of original reactants during recharging. It functions as galvanic cell and as electrolytic cell, as well.

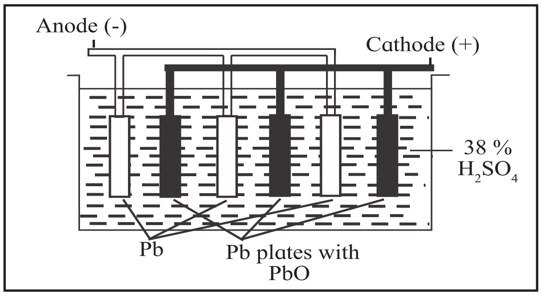
i. Construction :

a. A group of lead plates packed with spongy lead serves as anode (-). Another group of lead plates bearing lead dioxide (PbO_2) serves as cathode (+).

b. To provide large reacting surface, the cell contains several plates of each type. The two types of plates are alternately arranged.

c. The electrodes are immersed in an electrolytic aqueous solution of 38 % (by mass) of sulphuric acid of density 1.2 g/mL.

ii. Diagram :



Lead storage cell

Notation of the cell : The cell is formulated as $Pb_{(s)}|PbSO_{4(s)}|38\%H_2SO_{4(aq)}|PbSO_{4(s)}|PbO_{2(s)}|Pb(s)$.

iii. Cell reactions during discharge

a. Oxidation at anode (–) :

When the cell provides current, spongy lead is oxidised to Pb^{2-} ions and negative charge accumulates on lead plates.

The Pb^{2+} ions so formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble $PbSO_4$. The net oxidation is the sum of these two processes.

$$Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^- \qquad \text{(oxidation)}$$

$$Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} \qquad \text{(precipitation)}$$

$$Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^- ......(i) \qquad \text{(overall oxidation)}$$

b. Reduction at cathode (+) :

The electrons produced at anode travel through external circuit and re-enter the cell at cathode. At cathode PbO_2 is reduced to Pb^{2+} ions in presence of H^+ ions.

Subsequently Pb^{2+} ions so formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble $PbSO_4$ that gets coated on the electrode.

$$PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O(l) \qquad \text{(reduction)}$$

$$Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} \qquad \text{(precipitation)}$$

$$PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O(l)......(ii) \qquad \text{(overall oxidation)}$$

c. Net cell reaction during discharge:

The net cell reaction is the sum of overall oxidation at anode and overall reduction at cathode.

$$Pb_{(s)} + Pb_{2(s)} 4H^+_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O(l) \qquad \text{or}$$

$$Pb_{(s)} + Pb_{2(s)} 2H_2SO_{(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O(l) \qquad .....(iii)$$

As the cell operates to generate current, H_2SO_4 is consumed.
Its concentration (density) decreases and the cell potential is decreased. The cell potential thus depends on sulphuric acid concentration (density).

iv. Cell reactions during recharging :

The potential of lead accumulator is 2V. It must be recharged with the falling of the cell potential to 1.8 V.
To recharge the cell external potential slightly greater than 2 V needs to be applied across the electrodes.
During recharging the cell functions as electrolytic cell. The anode and cathode are interchanged with PbO_2 electrode being anode (+) and lead electrode cathode (–).

a. Oxidation at anode (+) :

It is reverse of reduction reaction (ii) at cathode that occurs during discharge.

$$PbSO_{4(s)} + 2H_2O(l) \longrightarrow PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \qquad ...(iv)$$

b. Reduction at cathode (-) :

It is reverse of oxidation reaction (i) at anode that occurs during discharge.

$$PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO^{2-}_{4(aq)} \qquad ...(v)$$

c. Net cell reaction : It is the sum of reaction (iv) and (v) or the reverse of net cell reaction (iii) that occurs during discharge

$$2PbSO_{4(s)} + 2H_2O(l) \longrightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$$

The above reaction shows that H_2SO_4 is regenerated. Its concentration (density) and in turn, the cell potential increases.

Q.88 What are the application of lead accumulator?

Ans:

i. It is used as a source of direct current in the laboratory.

ii. A 12 V lead storage battery constructed by connecting six 2 V cells in series is used in automobiles and inverters.

Q.89 Write the electrode reactions when lead storage cell generates electricity. What are the anode and cathode and write the electrode reactions during its recharging.

Ans:

i. Cell reaction when lead storage battery discharge:
Refer Q.92 (iii) – (a and b)
During recharging the anode and cathcode are interchanged with PbO_2 electrode being anode (+) and lead electrode cathode (–)

ii. Cell reaction when lead storage battery recharging:
Refer Q.92 (iv) – (a and b)

★Q.90 Why do the cell potential of lead accumulators decreases when it generates electricity? How the cell potential can be increased?

Ans:

i. The cell potential depends on sulphuric acid concentration. As the cell operates to generate current H_2SO_4 is consumed and its concentration decreases and the cell potential is decteased.

ii. During the recharging process by applying external potential slightly greater than 2V, H_2SO_4 is regenerated.
As a result, its concentration increases and in turn, the cell potential increases.

Q.91 Write a short note on Nickel cadmium or NICAD storage.

Ans:

i. Nickel-cadmium cell is a secondary dry cell. In other words it is a dry cell that can be recharged.

ii. Anode of the NICAD storage cell is cadmium metal. The cathode is nickel (IV) oxide, NiO_2 supported on Ni. The electrolyte solution is basic.

iii. The electrode reactions and overall cellreaction are as follows :

$$Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^- \text{ (oxidation)}$$

$$NiO_{2(s)} + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)} \text{ (precipitation)}$$

$$Cb_{(s)} + NiO_{2(s)} + 2H_2O(l) \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_2 \text{ (overall oxidation)}$$

iv. The reaction product at each electrode is solid that adheres to electrode surface. Therefore the cell can be recharged.

v. The potential of the cell is about 1.4 V. The cell has longer life than other dry cells.

vi. It can be used in electronic watches, calculators, photographic equipments, etc

★Q.92 Write the electrocle reactions and net cell reaction for NICAD storage.

Ans: *Refer Q.91 (iii)*

Q.93 Write a short note on mercury.

Ans:

i. Mercury battery is a secondary dry cell and can be recharged.

ii. The mercury battery consists of zinc anode,
amalgamated with mercury. The cathode is
a paste of Hg and carbon.

iii. The electrolyte is strongly alkaline and made of a paste of KOH and ZnO.

iv. The electrode ractions and net cell reaction are :

$$Zn_{(Hg)} + 2OH^-_{(aq)} \longrightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$$

(anode oxidation)

$$HgO_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow Hg_{(l)} + 2\,OH^-_{(aq)}$$

(cathode reduction)

$$Zn_{(Hg)} + Hg\,O_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$$

(overall cell reaction)

v. The overall reaction involves only solid substances. There is no change in electrolyte composition during operation.

vi. The mercury battery, therefore, provides more constant voltage (1.35V) than the Leclanche' dry cell.

vii. It also has considerably higher capacity and longer life than dry cell.

viii. Uses the mercury dry cell finds use in hearing aids, electric watches, pacemakers, etc.

Q.94 Give the advantage of mercury cells over dry cells.

Ans:

i. The overall reaction involves only solid substances. There is no change in electrolyte composition during operation.

ii. The mercury battery, therefore, provides more constant voltage (1.35V) than the Leclanche' dry cell.

iii. It also has considerably higher capacity and longer life than dry cell.

5.11 Fuel cells

Q.95 Explain the functioning of fuel cell.

Ans:

i. The functioning of fuel cells is based on the fact that combustion reactions are of redox type and can be used to generate electricity.

ii. The fuel cells differ from ordinary galvanic cells in that the reactants are not placed within the cell.

iii. They are continuously supplied to electrodes from a reservoir.

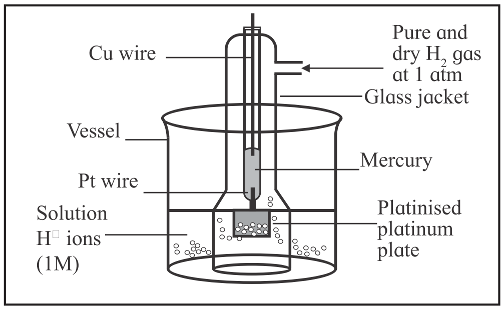
iv. In these cells one of the reactants is a fuel such as hydrogen gas or methanol.

v. The other reactant such as oxygen, is oxidant.

vi. The simplest fuel cell is hydrogen-oxygen fuel cell.

Q.96 Explain the construction of Hydrogen-oxygen fuel cell with help of a diagram and give its cell reaction.

Ans:



i. Hydrogen-oxygen fuel cell :

  a. In H_2 - O_2 fuel cell, the fuel is hydrogen gas. Oxygen gas is an oxidising agent.

  b. The energy of the combustion of hydrogen is converted into electrical energy.

ii. Construction :

  a. The anode and cathode are porous carbon rods containing small amount of finely divided platinum metal that acts as a catalyst.

  b. The electrolyte is hot aqueous solution of KOH.

  c. The carbon rods immersed into electrolyte

  d. Hydrogen gas is continuously bubbled, through anode and oxygen gas through cathode into the electrolyte.

iii. Cell reactions

  a. Oxidation at anode (-) : At anode hydrogen gas is oxidised to H_2O.

$$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O(l) + 4e^- \text{.........(i)}$$

  b. Reduction at cathode (+) : The electrons released at anode travel, through external circuit to cathode. Here O_2 is reduced to OH^-.

$$O_{2(g)} + 2H_2O_{(aq)} + 4e^- \rightarrow 4OH^-_{(aq)} \text{..........(ii)}$$

  c. Net cell reaction : The overall cell reaction is the sum of electrode reactions (i) and (ii).

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O\ (l) \text{............(iii)}$$

iv. The overall cell reaction is combustion of H_2

to form liquid water. Interestingly, the fuel H_2 gas and the oxidant O_2 do not react directly.

v. The chemical energy released during the formation of O-H bond is directly converted into electrical energy accompanying in above combustion reaction.

vi. The cell continues to operate as long as H_2 and O_2 gases are supplied to electrodes.

The cell potential is given by

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.4V - (-0.83V)$
$= 1.23$ V.

Q.97 What are anode and cathode of H_2–O_2 fuel? Name the electrolyte used in it. Write electrode reactions and net cell reaction taking place in the fuel cell.

Ans:

i. The anode and cathode are porous carbon rods containing small amount of finely divided platinum metal that acts as a catalyst.

ii. The electrolyte is hot aqueous solution of KOH.

Refer Q.96 (iii)

Q.98 What are the advantages of hydrogen - oxygen fuel cells.

Ans: Advantages of fuel cells

i. The reacting substances are continuously supplied to the electrodes. Unlike conventional galvanic cells, fuel cells do not have to be discarded on consuming of chemicals.

ii. They are non-polluting as the only reaction product is water.

iii. Fuel cells provide electricity with an efficiency of about 70 % which is twice as large when compared with efficiency of thermal plants (only 40 %).

Q.99 Give the drawbacks of hydrogen-oxygen fuel cells.

Ans: Drawbacks of hydrogen-oxygen fuel cells

i. H_2 is hazardous to handle

ii. Cost of preparing H_2 gas in high.

Q.100 Give the applications of fuel cells.

Ans:

i. The fuel cells are used on experimental basis in automobiles.

ii. The fuel cell are used for electrical power in the space programme.

iii. In space crafts the fuel cell is operated at such a high temperature that the water evaporates at the same rate as it is formed. The vapour is condensed and pure water formed is used for drinking by astronauts.

iv. In future, fuel cells can possibly be explored as power generators in hospitals, hotels and homes.

Can you recall?

+Q.101 In what ways are fuel cells and galvanic cells similar and in what ways are they different?

Ans:

i. Similarities between fuel cells and galvanic cells.
   a. In both the cells chemical energy is converted in electrical energy.
   b. In both the cells anode is negative and cathode is positive.
   c. In fuel cell and galvanic cells spontaneous redox type of reaction are used to generate electricity.

ii. Dissimilartities between fuel cells and galvanic cells.
   a. In galvanic cell the reactants are placed within the cell, but in the fuel cells, the reactants are not placed within the cell.
   b. In fuel cells, reactans are continuously supplied to electrode from a reservoir, whereas galvanic cells have to be discarded after consuming reactants.
   c. In fuel cells, the energy of combustion of hydrogen is converted into electrical energy.

5.12 Electrochemical series

Q.102 What is electrochemical or electromotive series?

Ans:

i. The standard potentials of a number of electrodes have been determined using standard hydrogen electrode. These electrodes with their half reactions are arranged according to their decreasing standard potentials

ii. This arrangement is called electrochemical series.

Q.103 What are the key points of electrochemical series?

Ans:

i. The half reactions are written as reductions. The oxidizing agents and electrons appear on the left side of half reactions while the reducing agents are shown on the right side in the half reaction.

ii. Below hydrogen electrode the negative standard potential increases and above hydrogen electrode the positive standard potential increases.

iii. E^0 values apply to the reduction half reactions that occur in the forward direction as written.

iv. Higher (more positive) E^0value for a half reaction indicates its greater tendency to occur in the forward direction and in turn greater tendency for the substance to reduce. Conversely, the low (more negative) E^0 value of a half reaction corresponds to its greater tendency to occur in the reverse direction or for the substance to oxidise.

Remember-

The left side of half reaction has cations of metals or non metallic molecules (oxidants). There are free metals or anions of non metals on the right side (reductants).

Q.104 What are the applications of electrochemical series?

Ans:

i. Relative strength of oxidising agents:

a. The species on the left side of half reactions are oxidizing agents. E^0 value is a measure of the tendency of the species to accept electrons and get reduced.

b. In other words, E^0 value measures the strength of the substances as oxidising agents. Larger the E^0 value greater is the oxidising strength.

c. The species in the top left side of half reactions are strong oxidising agents. As we move down the table, E^0 value and strength of oxidising agents decreases from top to bottom.

ii. Relative strength of reducing agents:

a. The species on the right side of half reactions are reducing agents.

b. The half reactions at the bottom of the table with large negative E^0 values have a little or no tendency to occur in the forward direction as written. They tend to favour the reverse direction.

c. It follows, that the species appearing at the bottom right side of half reactions associated with large negative E^0 values are the effective electron donors.

d. They serve as strong reducing agents. The strength of reducing agents increases from top to bottom as E^0 values decrease.

iii. Spontaneity of redox reactions :

a. A redox reaction in galvanic cell is spontaneous only if the species with higher E^0 value is reduced (accepts electrons) and that with lower E^0 value is oxidised (donates electrons).

b. The standard cell potential must be positivefor a cell reaction to be spontaneous under the standard conditions.

Electrode	Half reaction Left side species (oxidizing agents)		Half reaction Right side species (oxidizing agents)	E^0V
$F^-\|F_2\|$ Pt	↑ Increasing strength as oxidising agent	$F_2+2e^- \longrightarrow F^-$	↓ Increasing strength as reducing agent	+2.870
$Au^+\|Au$		$Au+e^- \longrightarrow Au$		+1.680
$Ce^{4+}, Ce^{3+}\|Pt$		$Ce^{4+}+e^- \longrightarrow Ce^{3+}$		+1.610
$Au^{3+}\|Au$		$Au^{3+}+3e^- \longrightarrow Au$		+1.500
$Cl^-\|Cl_2\|Pt$		$Cl_2+2e^- \longrightarrow 2Cl^-$		+1.360
$Pt^{2+}\|Pt$		$Pt^{2+}+2e^- \longrightarrow Pt$		+1.200
$Br^-\|Br_2\|Pt$		$Br_2+2e^- \longrightarrow 2Br^-$		+1.080
$Hg_2^{2+}\|Hg$		$Hg\ ^{2+}+2e^- \longrightarrow Hg$		+0.854
$Ag^+\|Ag$		$Ag^+e^- \longrightarrow Ag$		+0.799
$Hg_2^{2+}\|Hg$		$Hg_2^{2+}+2e^- \longrightarrow 2Hg$		+0.79
$Fe^{3+},Fe^{2+}\|Pt$		$Fe^{3+}e^- \longrightarrow Fe^{2+}$		+0.771
$I^-\|I_{2(s)}\|Pt$		$I_2+2e^- \longrightarrow 2I^-$		+0.535
$Cu^{2+}\|Cu$		$Cu^{2+}+2e^- \longrightarrow Cu$		+0.337
$Ag\|AgCl_{(s)}\|Cl^-$		$AgCl_{(s)}+e^- Ag+Cl^-$		+0.222
$Cu^{2+},Cu^+\|Pt$		$Cu^{2+}+e^- \longrightarrow Cu$		+0.153
$Sn^{4+},Sn^{2+}\|Pt$		$Sn^{4+}+2e^- \longrightarrow Sn^{2+}$		+0.15
$H^+\|H_2\|Pt$		$2H^++2e^- \longrightarrow H_2$		+0.00
$Pb^{2+}\|Pb$		$Pb_{2+}+2e^- \longrightarrow Pb$		-0.126
$Sn^{2+}\|Sn$		$Sn^{2+}+2e^- \longrightarrow Sn$		-0.136
$Ni^{2+}\|Ni$		$Ni^{2+}+2e^- \longrightarrow Ni$		-0.257
$Co^{2+}\|Co$		$Co^{2+}2e^- \longrightarrow Co$		-0.280
$Cd^{2+}\|Cd$		$Cd^{2+}+2e^- \longrightarrow Cd$		-0.403
$Fe^{2+}\|Fe$		$Fe^{2+}+2e^- \longrightarrow Fe$		-0.440
$Cr^{3+}\|Cr$		$Cr^{3+}+3e^- \longrightarrow Cr$		-0.740
$Zn^{2+}\|Zn$		$Zn^{2+}+2e^- \longrightarrow Zn$		-0.763
$Al^{3+}\|Al$		$Al^{3+}+3e^- \longrightarrow Al$		-1.66
$Mg^{2+}\|Mg$		$Mg^{2+}+2e^- \longrightarrow Mg$		-2.37
$Na^+\|Na$		$Na^++2e^- \longrightarrow Na$		-2.714
$Ca^{2+}\|Ca$		$Ca^{2+}+2e^- \longrightarrow Ca$		-2.866
$K^+\|K$		$K^++e^- \longrightarrow K$		-2.925
$Li^+\|Li$		$Li^++e^- \longrightarrow Li$		-3.045

Use your brain power.

+Q.105 Identify the strongest and the weakest oxidizing agents from the electrochemical series.

Ans: Fluorine (F_2) is the strongest oxidizing agent and lithium ion (Li^+) is weakest oxidising agent.

Use your brain power.

+Q.106 Identify the strongest and the weakest reducing agents from the electrochemical series.

Ans: Lithium (Li) is the strongest reducing agent and reducing agent and fluoride ion (F^-) is the weakest reducing agent.

+Q.107 Identify oxidising agents and arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.

{Al (– 1.66V), Al^{3+} (–1.66 V), Cl_2 (1.36 V), Cd^{2+} (– 0.44V), I_2 (0.54V), Br^- (1.09V)}

Ans: According to electrochemical series.

i. The species on the left hand side of the half reactions are oxidising agents. Thus, oxidising agents are Al^{3+}, Cl_2, Cd^{2+}, and I_2

ii. Larger the E^0 value greater is the strength of oxidising agent. Increasing strength of oxidising agents is as follows:

$$Al^{3+}_{(-1.66v)} < Cd^{2+}_{(-0.4V)} < I_{2(0.54V)} < Cl_{2(1.36V)}$$

Q.108 Which of the following species are reducing agents? Arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.

{K(– 2.93V), Br^2(1.09V), Ce^{3+}(1.61V), Ti^{2+} (– 0.37V), Ag^+ (0.8V), Ni(– 0.23V)}

Ans: According to electrochemcial series.

i. The species on the right hand side of the half reactions are reducing agents. Thus, reducing agents are
K, Mg, Ti^{2+}, Ni

ii. The strength of reducing agents increases as E^0 values decrease. Increasing strength of reducing agents is as follows.

$$Ni_{(-0.23V)} < Ti^{2+}_{(-0.37V)} < Mg_{(-2.36V)} < K_{(-2.93V)}$$

Type-5

Numericals based on electrochemical series

1. To answer this question, first we write oxidation of Mg by Ag^+.

Solution:

$$Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e^- \text{(oxidation)}$$
$$2Ag^{2+}{}_{(aq)} + 2e^- \rightarrow 2Ag_{(s)} \text{(reduction)}$$
$$\overline{Mg_{(s)} + 2Ag^{2+}{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + 2Ag_{(s)}}$$
$$\text{(overall reaction)}$$

From electrochemical series we have $E^0_{Mg} = –2.37$ V and $E^0_{Ag} = 0.8$ V. For the cell having Mg as anode and Ag cathode.

$E^0_{Cell} = E^0_{Ag} - E^0_{Mg} = 0.8V - (-2.37V)$
$= 3.17$ V.

EMF being positive the cell reaction is spontaneous. Thus Ag^+ ions oxidise to metallic Mg

2. Predict whther the following reactions would occur spontaneously under standard state conditions.

i. $\mathbf{Ca_{(S)} + Cd^{2+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + Cd_{(S)}}$

ii. $\mathbf{2Br^-_{(aq)} + Sn^{2+}_{(aq)} \rightarrow Br_{2_{(l)}} + Sn_{(s)}}$

iii. $\mathbf{2Ag_{(s)} + Ni^{2+}_{(aq)} \rightarrow 2Ag^{2+}_{(aq)} + Ni_{(s)}}$

Solution:

i. $Ca_{(S)} + Cd^{2+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + Cd_{(S)}$

At anode : $Ca_{(s)} \rightarrow Ca^{2+}_{(aq)} + 2e^-$

At cathode: $Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$

From the electrochemical series we have,
$E^0_{Ca} = -2.866$ V and $E^0_{Cd} = -0.403$V
For cell having Ca as anode and Cd as chthode.
$E^0_{cell} = E^0_{Cd} - E^0_{Ca} = -0.403\text{ V} - (-2.866)\text{V}$
$E^0_{cell} = 2.463$ V
Emf cell being positive, the given cell reaction is spontaneous.

ii. $2Br^-_{(aq)} + Sn^{2+}_{(aq)} \rightarrow Br_{2_{(l)(s)}} + Sn_{(s)}$

At anode: $2Br^-_{(aq)} \rightarrow Br_{2_{(l)}} + 2e^-$

At cathode: $Sn^{2+}_{(aq)} 2e^- \rightarrow Sn_{(s)}$

From the electrochemical series we have,

$E^0_{Br_2} = 1.080V$ and $E^0_{Sn} = -0.136V$

For cell having $Br_{2_{(l)}}$ as anode and Sn as cathode.

$$E^0_{cell} = E^0_{Sn} - E^0_{Br_2} = -0.136V - 1.080V$$

$$E^0_{cell} = -1.0216V$$

Emf of cell being negative, the given cell reaction is non-spontaneous.

iii. $2Ag_{(s)} + Ni^{2+}_{(aq)} \rightarrow 2Ag^+_{(aq)} + Ni_{(s)}$

At anode: $2Ag_{(s)} \rightarrow 2Ag^+_{(aq)} + 2e^-$

At cathode : $Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$

Form the electrochemical series we have,

$E^0_{Ag} = 0.799V$

$E^0_{Ni} = -0.257V$

For cell having Ag as anode and Ni as cathode.

$E^0_{cell} = E^0_{Ni} - E^0_{Ag} = -0.257V - 0.799V$

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