

5. ELECTROCHEMISTRY

Can you recall ?

- What is a redox reaction ?
- Which form of energy is converted into electrical energy in dry cells ?



- How is NaOH manufactured from NaCl ?

5.1 Introduction : Dry cell is used to power our electrical and electronic equipments because it generates electricity. Do you know how does a dry cell generate electricity ? A chemical reaction occurs in it which generates electricity. Thus in a dry cell chemical energy is converted into electrical energy.

You are familiar with the electrolysis of solutions of ions. Electrolysis is breaking down of an ionic compound by the passage of electricity. Breaking down of an electrolyte during electrolysis is a chemical reaction that takes place by the passage of electricity. Electrical energy is, thus, converted into chemical energy.

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

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. (Refer to Chapter 3).

The study of electrochemical cells is important in science and technology. It

makes possible the manufacture of essential chemicals. You have learnt preparation of NaOH, widely used in the manufacture of soaps, detergents and paper, by electrolysis of NaCl. Electrolysis is possibly the only means to produce fluorine. 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.

In standard XI, you learnt redox reactions. Redox reaction forms the basis for the generation of electricity by chemical reactions and also for chemical reactions brought out by means of electricity. These processes are carried out in an **electrochemical cell**. Electrochemistry deals with the design and operation of such cells.

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.

5.2 Electric conduction : We know that the electric current represents a charge transfer. A charge transfer or flow of electricity occurs through substances called conductors. There are two types of conductors which give rise to two types of conduction of electricity.

5.2.1 Metallic conduction :

Can you recall ?

- What is the origin of electrical conductivity of metals ?



Electrical conduction through metals involves a direct flow of electrons from one point to the other. The outermost electrons of metals form conduction band. The electrons in conduction band are free to move and hence flow under the influence of applied electrical potential (Chapter 1). Metallic conductors are, thus, electronic conductors.

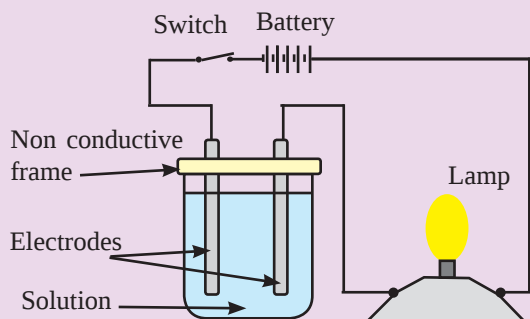
5.2.2 Electrolytic or ionic conduction :

Electrolytic conduction involves conduction of electric current by the movement of ions of the electrolytes. 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. Substances such as ionic salts, strong or weak acids and bases are the electrolytes. These dissociate into ions when dissolved in polar solvents such as water. Ionic solids dissociate into ions in molten state as well.

Conduction through electrolytic conductors involves transfer of matter from one part of the conductor to the other. It means that the current flowing through an electrolytic conductor is accompanied by a chemical change.

5.2.3 Information provided by measurement of conductivities of solutions :

Try this...



- Arrange a simple set up as shown in the diagram above.
- The lamp will glow when circuit is complete.
- Prepare 5 % (mass/volume) solutions of cane sugar, acetic acid, sodium chloride and urea in distilled water.
- Check the electrical conductivity of these solutions using the above assembly. Compare these with that observed with distilled water.

- The conducting and nonconducting nature of solutions can be identified by measurement of their conductivity. Sucrose and urea do not dissociate in their aqueous solutions. The conductivities of these solutions are nearly the same as that of water. These substances are called **nonelectrolytes**.

On the other hand, substances like potassium chloride, acetic acid, sodium hydroxide, HCl dissociate in their aqueous solutions. 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.

- On the basis of high or low electrical conductivity electrolytes are classified into strong and weak electrolytes. The substances such as ionic salts, strong acids or bases are almost completely dissociated in aqueous solutions. These are strong electrolytes. The solutions of **strong electrolytes** exhibit high conductivities.

The weak acids and weak bases are **weak electrolytes**. They dissociate to a very small extent in aqueous solutions and show lower conductivities 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 :

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 :

$$R = \frac{V}{I} \quad \dots\dots\dots (5.1)$$

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

electrical resistance is ohm denoted by the symbol Ω (omega). Thus, $\Omega = \text{VA}^{-1}$.

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

$$G = \frac{1}{R} \quad \dots\dots\dots (5.2)$$

The SI unit of G is siemens, denoted by S, which is equal to Ω^{-1} . Therefore, we write $S = \Omega^{-1} = \text{AV}^{-1} = \text{CV}^{-1}\text{s}^{-1}$ where C represents coulomb, the unit of electricity related to current strength in ampere and time in seconds as $C = \text{A s}$.

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

$$R \propto \frac{l}{a} \text{ or } R = \rho \frac{l}{a} \quad \dots\dots\dots (5.3)$$

where ρ , the proportionality constant is called resistivity of the conductor. It is the resistance of conductor of unit length and unit cross sectional area.

Can you recall ?

What is the SI unit of resistivity ?



5.3.1 Conductivity (k) : We have seen that $G = 1/R$ and R is directly proportional to length and inversely proportional to its cross sectional area. It, therefore, follows that G is directly proportional to a and inversely proportional to the length l . Thus

$$G \propto \frac{a}{l} \text{ or } G = k \frac{a}{l} \quad \dots\dots\dots (5.4)$$

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

Thus, conductivity is the electrical conductance of a conductor of unit length and unit area of cross section. In other words, the conductivity is the electrical conductance of unit cube of material. 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.

From Eq. (5.2) and Eq. (5.4), we write

$$k = G \frac{l}{a} = \frac{1}{R} \frac{l}{a} \quad \dots\dots\dots (5.5)$$

Combination of Eq. (5.3) and Eq. (5.5) shows that $k = 1/\rho$.

Units of electrolytic conductivity

Quantity	SI unit	Common unit
Length	m	cm
Area	m^2	cm^2
Resistance	Ω	Ω
Conductivity	$\Omega^{-1} \text{ m}^{-1}$ or S m^{-1}	$\Omega^{-1} \text{ cm}^{-1}$

5.3.2 Molar conductivity ($\wedge$) : The electrolytic conductivity is not suitable for comparing conductivities of different solutions. The conductivity of a solution depends on number of ions present in unit volume of solution. The solution of higher concentration contains more ions and exhibits higher conductivity than the solution of lower concentration. To compare conductivities of different solutions, they must have the same concentration.

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

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

$$\wedge = \frac{k}{c} \quad \dots\dots\dots (5.6)$$

SI units of k are S m^{-1} and that of c are mol m^{-3} . Hence SI units of $\wedge$ are $\text{S m}^2 \text{ mol}^{-1}$. Common units employed for molar conductivity are $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Significance of molar conductivity : To understand the significance of $\wedge$, 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. The electrical conductance exhibited by this solution is the molar conductivity. 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 cm³ 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.



5.3.3 Relation between k and $\wedge$: Conductivity k is the electrical conductance of 1 cm³ of solution. If V is volume of solution in cm³ containing 1 mole of dissolved electrolyte, its electrical conductance is $\wedge$. Each 1 cm³ portion in the volume V has conductance k . Hence, total conductance of V cm³ is kV which is molar conductivity.

Thus, we have $\wedge = kV$ (5.7)

Concentration of solution

$$= c \text{ mol L}^{-1}$$

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

Volume, V of solution in cm³ containing 1 mole of an electrolyte is reciprocal of concentration. Therefore,

$$V = \frac{1}{\text{concentration}} = \frac{1000}{c} \text{ cm}^3 \text{ mol}^{-1} \text{ (5.8)}$$

Substitution for V in Eq. (5.7) yields

$$\wedge = \frac{1000k}{c} \text{ (5.9)}$$

Try this...

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



Problem 5.1 : The molar conductivity of 0.05 M BaCl₂ solution at 25°C is 223 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. What is its conductivity ?

Solution :

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

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

Hence

$$k = \frac{223 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \times 0.05 \text{ mol L}^{-1}}{1000 \text{ cm}^3 \text{L}^{-1}} = 0.01115 \Omega^{-1} \text{ cm}^{-1}$$

5.3.4 Variation of conductivity with concentration

- The electrolytic conductivity is electrical conductance of unit volume (1 cm³) of solution. It depends on the number of current carrying ions present in unit volume of solution.
- On dilution total number of ions increase as a result of increased degree of dissociation.
- 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.

Suppose 100 cm³ of solution of an electrolyte contains 8×10^{20} ions. The number of ions per cm³ is 8×10^{18} .

If the solution is diluted to 1000 cm³ 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 cm³ is 6.4×10^{18} .

It is evident that the number of ions per cm³ decreases from 8×10^{18} to 6.4×10^{18} on dilution from 100 cm³ to 1000 cm³ and in turn, the conductivity decreases.

5.3.5 Variation of molar conductivity with concentration

- The molar conductivity is the electrical conductance of 1 mole of an electrolyte in a given volume of solution.
- The increasing number of ions produced in solution by 1 mole of the electrolyte lead to increased molar conductivity.

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

i. Strong electrolytes : The molar conductivity of solution of strong electrolyte increases rapidly with dilution. 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 Λ_0 . The zero concentration or infinite dilution means the solution is so dilute that further dilution does not increase the molar conductivity.

During nineteenth century F. Kohlrausch with repeated experiments showed that the molar conductivity of strong electrolytes varies linearly with square root of concentration as :

$$\Lambda = \Lambda_0 - a \sqrt{c} \quad \dots\dots\dots (5.10)$$

where a is constant. For strong electrolytes a plot of Λ versus $\sqrt{c}$ is linear as shown in Fig. 5.1.

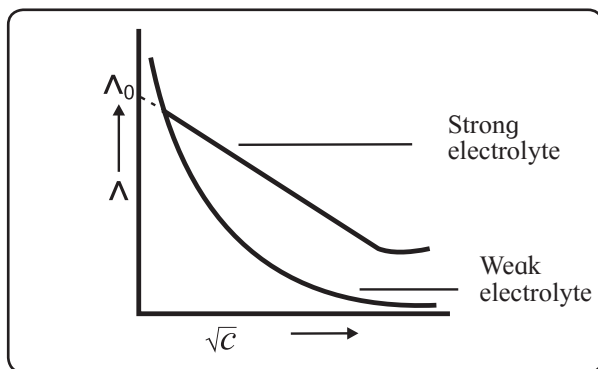


Fig. 5.1 : Variation of Λ with $\sqrt{c}$

ii. Weak electrolytes : The molar conductivity of weak electrolytes increases rapidly on dilution. For concentrations of 0.001M or 0.0001 M, the Λ value is lower than Λ_0 the molar conductivity at zero concentration.

For weak electrolytes the variation of Λ with $\sqrt{c}$ shown in Fig. 5.1 is not linear.

Molar conductivity of strong electrolytes at zero concentration can be determined by extrapolation of linear part of Λ versus $\sqrt{c}$ curve as shown in Fig. 5.1. This method cannot be used for weak electrolytes since Λ versus $\sqrt{c}$ curve does not approach linearity. Kohlrausch law is useful for calculating Λ_0 of weak electrolytes.

5.3.7 Kohlrausch law of independent migration of ions : The law states that at infinite dilution each ion migrates independent of co-ion and contributes to total molar conductivity of an electrolyte irrespective of the nature of other ion to which it is associated.

Both cation and anion contribute to molar conductivity of the electrolyte at zero concentration and thus Λ_0 is sum of molar conductivity of cation and that of the anion at zero concentration. Thus,

$$\Lambda_0 = n_{\oplus} \lambda_{\oplus}^0 + n_{\ominus} \lambda_{\ominus}^0 \quad \dots\dots\dots (5.11)$$

where $\lambda_{\oplus}$ and $\lambda_{\ominus}$ are molar conductivities of cation and anion, respectively, and $n_{\oplus}$ and $n_{\ominus}$ are the number of moles of cation and anion, specified in the chemical formula of the electrolyte.

Applications of Kohlrausch theory

1. The theory can be used to calculate the molar conductivity of an electrolyte at the zero concentration. For example,

$$\Lambda_0(\text{KCl}) = \lambda_{\text{K}^{\oplus}}^0 + \lambda_{\text{Cl}^{\ominus}}^0$$

$$\Lambda_0[\text{Ba}(\text{OH})_2] = \lambda_{\text{Ba}^{2\oplus}}^0 + 2 \lambda_{\text{OH}^{\ominus}}^0$$

Knowing the molar conductivities of ions at infinite dilution, Λ_0 values of electrolyte can be obtained.

2. The theory is particularly useful in calculating Λ_0 values of weak electrolytes from those of strong electrolytes. For example, Λ_0 of acetic acid can be calculated by knowing those of HCl, NaCl and CH_3COONa as described below :

$$\Lambda_0(\text{HCl}) + \Lambda_0(\text{CH}_3\text{COONa}) - \Lambda_0(\text{NaCl})$$

$$= \lambda_{\text{H}^{\oplus}}^0 + \lambda_{\text{Cl}^{\ominus}}^0 + \lambda_{\text{CH}_3\text{COO}^{\ominus}}^0 + \lambda_{\text{Na}^{\oplus}}^0 - \lambda_{\text{Na}^{\oplus}}^0 - \lambda_{\text{Cl}^{\ominus}}^0$$

$$= \lambda_{\text{H}^{\oplus}}^0 + \lambda_{\text{CH}_3\text{COO}^{\ominus}}^0 = \Lambda_0(\text{CH}_3\text{COOH})$$

Thus,

$$\Lambda_0(\text{CH}_3\text{COOH}) = \Lambda_0(\text{HCl}) + \Lambda_0(\text{CH}_3\text{COONa}) - \Lambda_0(\text{NaCl})$$

Because Λ_0 values of strong electrolytes, HCl, CH₃COONa and NaCl, can be determined by extrapolation method, the Λ_0 of acetic acid can be obtained.

Problem 5.2 : Calculate the molar conductivity of AgI at zero concentration if the molar conductivities of NaI, AgNO₃ and NaNO₃ at zero concentration are respectively, 126.9, 133.4 and 121.5 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Solution :

According to Kohrausch law,

$$\begin{aligned} \text{i. } \Lambda_0(\text{NaI}) &= \lambda_{\text{Na}^{\oplus}}^0 + \lambda_{\text{I}^{\ominus}}^0 \\ &= 126.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{ii. } \Lambda_0(\text{AgNO}_3) &= \lambda_{\text{Ag}^{\oplus}}^0 + \lambda_{\text{NO}_3^{\ominus}}^0 \\ &= 133.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{iii. } \Lambda_0(\text{NaNO}_3) &= \lambda_{\text{Na}^{\oplus}}^0 + \lambda_{\text{NO}_3^{\ominus}}^0 \\ &= 121.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

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

$$\begin{aligned} &\Lambda_0(\text{NaI}) + \Lambda_0(\text{AgNO}_3) - \Lambda_0(\text{NaNO}_3) \\ &= \lambda_{\text{Na}^{\oplus}}^0 + \lambda_{\text{I}^{\ominus}}^0 + \lambda_{\text{Ag}^{\oplus}}^0 + \lambda_{\text{NO}_3^{\ominus}}^0 - \lambda_{\text{Na}^{\oplus}}^0 - \lambda_{\text{NO}_3^{\ominus}}^0 \\ &= \lambda_{\text{Ag}^{\oplus}}^0 + \lambda_{\text{I}^{\ominus}}^0 \\ &= \Lambda_0(\text{AgI}) \\ &= 126.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 133.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &\quad - 121.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &= 138.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

Try this...

Calculate $\Lambda_0(\text{CH}_2\text{ClCOOH})$ if Λ_0 values for HCl, KCl and CH₂ClCOOK are respectively, 4.261, 1.499 and 1.132 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.



Problem 5.3 : Calculate molar conductivities at zero concentration for CaCl₂ and Na₂SO₄. Given : molar ionic conductivities of Ca²⁺, Cl⁻, Na⁺ and SO₄²⁻ ions are respectively, 104, 76.4, 50.1 and 159.6 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Solution :

According to Kohrausch law,

$$\begin{aligned} \text{i. } \Lambda_0(\text{CaCl}_2) &= \lambda_{\text{Ca}^{2+}}^0 + 2\lambda_{\text{Cl}^{\ominus}}^0 \\ &= 104 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} + 2 \times 76.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &= 256.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{ii. } \Lambda_0(\text{Na}_2\text{SO}_4) &= 2\lambda_{\text{Na}^{\oplus}}^0 + \lambda_{\text{SO}_4^{2-}}^0 \\ &= 2 \times 50.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &\quad + 159.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \\ &= 259.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

Problem 5.4 : The molar conductivity of 0.01M acetic acid at 25 °C is 16.5 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. 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 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Solution :

The degree of dissociation,

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

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

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

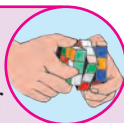
5.3.8 Molar conductivity and degree of dissociation of weak electrolytes : The degree of dissociation (α) of weak electrolyte is related to its molar conductivity at a given concentration c by the equation,

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \quad \dots\dots\dots (5.12)$$

where Λ_c is the molar conductivity of weak electrolyte at concentration c ; Λ_0 is molar conductivity at zero concentration.

Try this...

Obtain the expression for dissociation constant in terms of $\wedge_c$ and $\wedge_0$ using Ostwald's dilution law.



5.3.9 Measurement of conductivity : The conductivity of a solution can be determined from the resistance measurements by Wheatstone bridge.

Conductivity Cell : The conductivity cell consists of a glass tube with two platinum plates coated with a thin layer of finely divided platinum black. This is achieved by the electrolysis of solution of chloroplatinic acid. The cell is dipped in a solution whose resistance is to be measured as shown in Fig. 5.2.

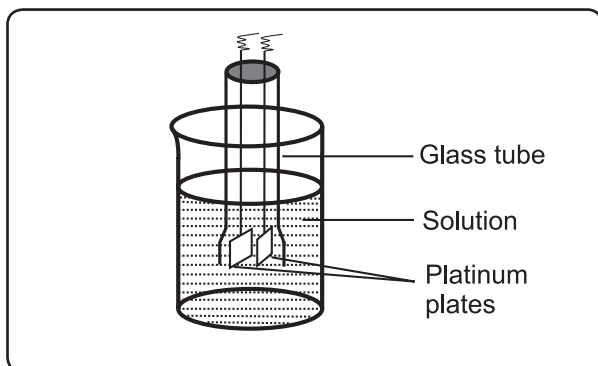


Fig. 5.2 : Conductivity cell

Cell constant : The conductivity of an electrolytic solution is given by Eq. (5.5),

$$k = \frac{1}{R} \frac{l}{a}$$

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. Thus,

$$\text{Cell constant} = \frac{l}{a} \quad \dots\dots\dots (5.13)$$

SI unit of cell constant is m^{-1} which is conveniently expressed in cm^{-1} . The Eq. (5.5) then becomes

$$k = \frac{\text{cell constant}}{R} \quad \dots\dots\dots (5.14)$$

The determination of molar conductivity consists of three steps :

1. Determination of cell constant : The cell constant is determined using the 1 M, 0.1 M or 0.01 M KCl solutions. The conductivity of KCl solution is well tabulated at various temperatures. The resistance of KCl solution is measured by Wheatstone bridge. (Refer to standard XII Physics Textbook Chapter 9)

In Fig. 5.3 AB is the uniform wire. R_x is the variable known resistance placed in one arm of Wheatstone bridge.

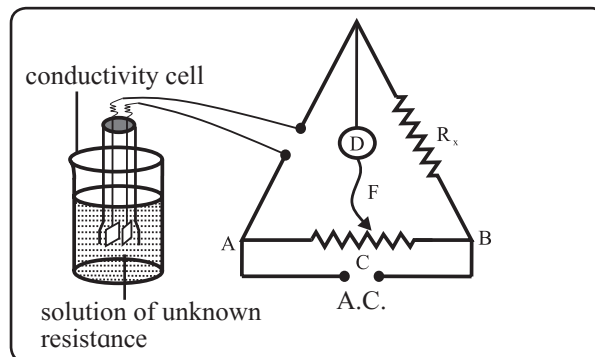


Fig. 5.3 : Measurement of resistance

The conductivity cell containing KCl solution of unknown resistance is placed in the other arm of Wheatstone bridge. D is a current detector. F is the sliding contact that moves along AB. A.C. represents the source of alternating current.

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.

According to Wheatstone bridge principle,

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

$$\text{Hence, } R_{\text{solution}} = \frac{l(AC)}{l(BC)} \times R_x \quad \dots\dots\dots (5.15)$$

By measuring lengths AC and BC and knowing R_x , resistance of KCl solution can be calculated. The cell constant is given by Eq. (5.13).

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

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

2. Determination of conductivity of given solution : KCl solution in the conductivity cell in step (1) is replaced by the given solution whose conductivity is to be measured. Its resistance is measured by the process described in step (1). The conductivity of given solution is then calculated as :

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

3. Calculation of molar conductivity : The molar conductivity of the given solution is then calculated using Eq. (5.9).

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

Problem 5.5: A conductivity cell containing 0.01M KCl gives at 25°C the resistance of 604 ohms. The same cell containing 0.001M AgNO₃ gives resistance of 6530 ohms. Calculate the molar conductivity of 0.001M AgNO₃. [Conductivity of 0.01M KCl at 25 °C is 0.00141 Ω⁻¹ cm⁻¹]

Solution :

i. Calculation of cell constant

$$\begin{aligned}\text{Cell constant} &= k_{\text{KCl}} \times R_{\text{KCl}} \\ &= 0.00141 \Omega^{-1} \text{ cm} \times 604 \Omega \\ &= 0.852 \text{ cm}^{-1}\end{aligned}$$

ii. Calculation of conductivity of AgNO₃,

$$\begin{aligned}k &= \frac{\text{Cell constant}}{R} \quad \text{where } R = 6530 \Omega \\ &= \frac{0.852 \text{ cm}^{-1}}{6530 \Omega} \\ &= 1.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}\end{aligned}$$

iii. Calculation of molar conductivity of AgNO₃

$$\begin{aligned}\Lambda &= \frac{1000k}{c} \quad \text{where } c = 0.001 \text{ M} \\ &= \frac{1000 \text{ cm}^3 \text{ L}^{-1} \times 1.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}}{0.001 \text{ mol L}^{-1}} \\ &= 130 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

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

5.4.1 Electrochemical reactions :

Can you recall ?

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



The chemical reaction occurring in electrochemical cells involves transfer of electrons from one species to the other. It is a redox reaction, we learnt in (Std. XI, Chapter 6).

Electrochemical reactions, are made of oxidation and reduction half reactions. The oxidation half reaction occurs at one electrode and the reduction half reaction occurs at the other electrode. The net cell reaction is the sum of these half reactions.

5.4.2 Electrodes : Electrodes are the surfaces on which oxidation and reduction half reactions take place. Electrodes may or may not participate in the reactions. The electrodes which do not take part in reactions are inert electrodes.

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

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

5.4.3 Types of electrochemical cells : There are two types of electrochemical cells.

1. Electrolytic cell : 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 such cells electrical energy is converted into chemical energy. The anode of electrolytic cell is positive and cathode is negative.

2. Galvanic or voltaic cell : In galvanic (voltaic) cell a spontaneous chemical reaction produces electricity. In these cells chemical energy is converted into electrical energy. The anode of galvanic cell is negative and cathode is positive.

Use your brain power

Distinguish between electrolytic and galvanic cells.



5.5 Electrolytic cell

Do you know ?

Michael Faraday was the first person to explain electrolysis nearly 200 years ago.



Electrolytic cell consists of a container in which electrolyte is placed. Two electrodes are immersed in the electrolyte and connected to a source of direct current.

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

Remember...

Electrolysis is the process of breaking down of an ionic compound in molten state or in aqueous solution by the passage of electricity.



5.5.1 Electrolysis of molten NaCl

Construction of cell : The electrolytic cell consists of a container in which fused NaCl is placed. Two graphite electrodes are immersed in it. They are connected by metallic wires to a source of direct current that is battery. This is shown in Fig. 5.4.

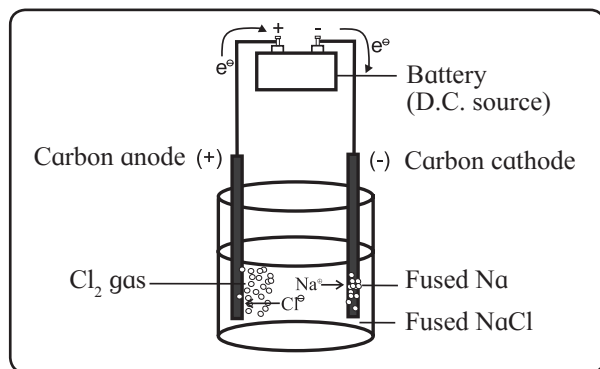


Fig. 5.4 : Electrolysis of fused NaCl

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

Remember...

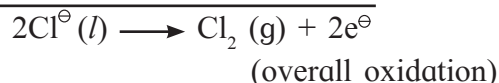
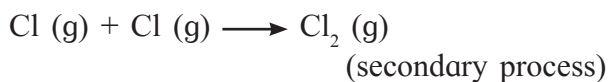
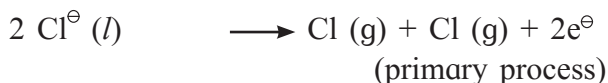
In electrolysis the electrodes are usually inert, Pt or graphite.



Reactions occurring in the cell : Fused NaCl contains Na^+ and Cl^- ions which are freely mobile. 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. When these ions reach the respective electrodes, they are discharged according to the following reactions.

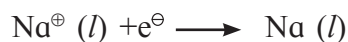
Oxidation half reaction at anode :

Cl^- ions migrate to anode. Each Cl^- ion, that reaches anode, gives one electron to anode. It oxidises to neutral Cl atom in the primary process. Two Cl atoms then combine to form chlorine gas in the secondary process.



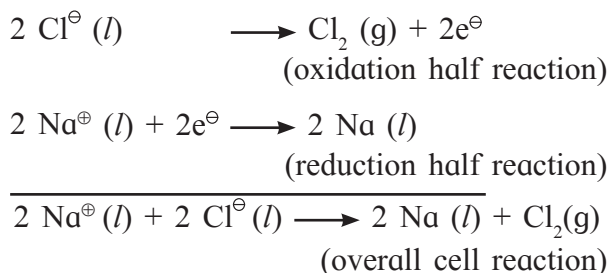
The battery sucks electrons so produced at the anode and pushes them to cathode through a wire in an external circuit. The battery thus serves as an electron pump. The electrons from the battery enter into solution through cathode and leave the solution through anode.

Reduction half reaction at cathode : The electrons supplied by the battery are used in cathodic reduction. Each Na^+ ion, that reaches cathode accepts an electron from the cathode and reduces to metallic sodium.



Net cell reaction

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



Results of electrolysis of molten NaCl

- A pale green Cl_2 gas is released at anode.
- A molten silvery-white sodium is formed at cathode.

Decomposition of NaCl into metallic sodium and $\text{Cl}_2(g)$ is nonspontaneous. The electrical energy supplied by the battery forces the reaction to occur.

Remember...

When molten ionic compound is electrolysed, a metal is formed at the negative electrode and a nonmetal at the positive electrode.



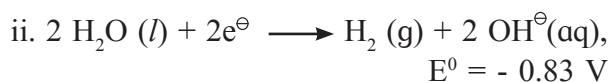
5.5.2 Electrolysis of aqueous NaCl :

Electrolysis of an aqueous NaCl can be carried out in the cell used for the electrolysis of molten NaCl using inert electrodes shown in Fig. 5.4. The fused NaCl is replaced by moderately concentrated aqueous solution of NaCl. The water involved in electrolysis of aqueous NaCl, leads to electrode reactions that differ from electrolysis of molten NaCl.

Reduction half reaction at cathode : At cathode, two reduction reactions compete. One is the reduction of $\text{Na}^{\oplus}$ ions as in case of molten NaCl.

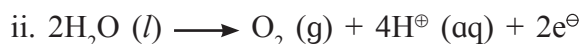
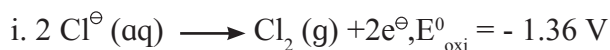


The other is the reduction of water to hydrogen gas.



The standard potential (section 5.7.1) for the reduction of water is higher than that for reduction of $\text{Na}^{\oplus}$. This implies that water has much greater tendency to get reduced than the $\text{Na}^{\oplus}$ ion. Hence reaction (ii), that is, reduction of water is the cathode reaction when the aqueous NaCl is electrolysed.

Oxidation half reaction at anode : At anode there will be competition between oxidation of $\text{Cl}^{\ominus}$ ion to Cl_2 gas as in case of molten NaCl and the oxidation of water to O_2 gas.



$$E^0_{\text{oxi}} = -0.4 \text{ V}$$

Standard electrode potential for the oxidation of water is greater than that of $\text{Cl}^{\ominus}$ ion or water has greater tendency to undergo oxidation. It is, therefore, expected that anode half reaction would be oxidation of water. The experiments have shown, however, that the gas produced at the anode is Cl_2 and not O_2 . This suggests that anode reaction is oxidation of $\text{Cl}^{\ominus}$ to Cl_2 gas. This is because of the overvoltage, discussion of which is beyond the scope of the present book.

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.

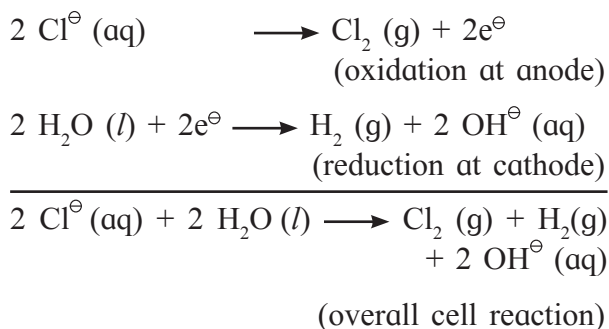
Do you know ?

Refining of metal and electroplating are achieved by electrolysis.



Overall cell reaction

It is the sum of electrode reactions.



Results of electrolysis of aqueous NaCl

- H_2 gas is liberated at cathode.
- Cl_2 gas is released at anode.
- Because $\text{Na}^{\oplus}$ ions remain unreacted and $\text{OH}^{\ominus}$ ions are formed at cathode, NaCl solution is converted to NaOH solution.

Do you know ?

Sea water is the source of 300000 tones of Mg produced every year by electrolysis.

Electrochemical art : Al, Cr and Sn can be coloured by an electrochemical process called anodizing. In this process metal anode oxidizes to give metal oxide coat. When an organic dye is added to the electrolyte, dye molecules soak forming spongy surface of coating and become trapped with the hardening of the metal oxide surface.



5.5.3 Quantitative aspects of electrolysis :

a. The mass of reactant consumed or the mass of product formed at an electrode during electrolysis can be calculated by knowing stoichiometry of the half reaction at the electrode.

i. Calculation of quantity of electricity passed : 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.

$$Q (\text{C}) = I (\text{A}) \times t (\text{s}) \quad \dots\dots\dots (5.16)$$

ii. Calculation of moles of electrons passed

Total charge passed is $Q(\text{C})$. The charge of one mole electrons is 96500 coulombs (C). It is referred to as one faraday (1 F). Hence,

$$\begin{array}{l} \text{Moles of electrons actually passed} \\ = \frac{Q(\text{C})}{96500 (\text{C/mol e}^{\ominus})} \quad \dots\dots\dots (5.17) \end{array}$$

iii. Calculation of moles of product formed

The balanced equation for the half reaction occurring at the electrode is devised. The stoichiometry of half reaction indicates the moles of electrons passed and moles of the product formed. For the reaction,

$\text{Cu}^{2\oplus} (\text{aq}) + 2\text{e}^{\ominus} \longrightarrow \text{Cu} (\text{s})$, two moles of electrons are required for the production of one mole of Cu. So we can calculate the moles of product formed. The moles of electrons actually passed are given by Eq. (5.16).

To simplify further we introduce the entity mole ratio given by

$$\begin{array}{l} \text{Mole ratio} = \\ \frac{\text{moles of product formed in the half reaction}}{\text{moles of electrons required in the half reaction}} \end{array}$$

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

Therefore,

Moles of product formed

$$= \text{moles of electrons actually passed} \times \text{mole ratio}$$

$$= \frac{Q(\text{C})}{96500 (\text{C/mol e}^{\ominus})} \times \text{mole ratio} \quad \dots\dots\dots (5.18)$$

$$= \frac{I (\text{A}) \times t (\text{s})}{96500 (\text{C/mol e}^{\ominus})} \times \text{mole ratio} \quad \dots\dots\dots (5.19)$$

iv. Calculation of mass of product :

Mass of product

$$W = \text{moles of product} \times \text{molar mass of product}$$

$$= \frac{I (\text{A}) \times t (\text{s})}{96500 (\text{C/mol e}^{\ominus})} \times \text{mole ratio} \times \text{molar mass of product} \quad \dots\dots\dots (5.20)$$

b. Suppose two cells containing different electrolytes are connected in series. The same quantity of electricity is passed through them. The masses of the substances liberated at the electrodes of the two cells are related as given below :

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

$$W_1 = \frac{Q(C)}{96500 (C/mol e^-)} \times (\text{mole ratio})_1 \times M_1$$

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

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

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

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

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

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

We have

$$\frac{W_1}{(\text{mole ratio})_1 \times M_1} = \frac{W_2}{(\text{mole ratio})_2 \times M_2} \quad \dots\dots\dots (5.21)$$

Problem 5.6 : 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 $\text{Cu}^{2+}(\text{aq}) + 2 e^- = \text{Cu}(\text{s})$

Hence,

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

ii. Mass of Cu formed,

$$\begin{aligned} W &= \frac{I (A) \times t (s)}{96500 (C/mol e^-)} \times \text{mole ratio} \times \text{molar mass of Cu} \\ &= \frac{5 A \times 100 \times 60 s}{96500 (C/mol e^-)} \times \frac{1 \text{ mol}}{2 \text{ mol } e^-} \\ &\quad \times 63.5 \text{ g mol}^{-1} \\ &= 9.87 \text{ g} \end{aligned}$$

Problem 5.7 : How long will it take to produce 2.415 g 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 :



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

ii. $W =$

$$\begin{aligned} &\frac{I (A) \times t (s)}{96500 (C/mol e^-)} \times \text{mole ratio} \times \text{molar mass of Ag} \\ 2.415 \text{ g} &= \frac{3 A \times t}{96500 (C/mol e^-)} \times \frac{1 \text{ mol}}{1 \text{ mol } e^-} \\ &\quad \times 107.9 \text{ g mol}^{-1} \end{aligned}$$

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

$$= 720 \text{ s} = 12 \text{ min.}$$

Do you know ?

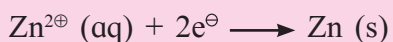
Names, galvanic or voltaic are given in honour of Italian scientists L. Galvani and A. Volta for their work in electrochemistry.



Problem 5.8 : 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



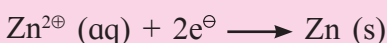
The equation shows that 1 mole of Zn^{2+} is reduced to Zn by 2 moles of electrons. For reduction of 3 moles of Zn^{2+} 6 moles of electrons will be required.

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.

Problem 5.9 : In a certain electrolysis experiment 4.36 g 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.

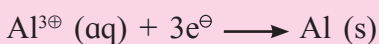
Solution :

Cell 1 :



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

Cell 2 :



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

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

$$W_1 = 4.36 \text{ g}, M_1 = 65.4 \text{ g mol}^{-1},$$

$$M_2 = 27 \text{ g mol}^{-1}$$

Substitution of the quantities gives

$$\frac{4.36 \text{ g}}{1 \text{ mol}/2 \text{ mol e}^{-} \times 65.4 \text{ g mol}^{-1}} = \frac{W_2}{1 \text{ mol}/3 \text{ mol e}^{-} \times 27 \text{ g mol}^{-1}}$$

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

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

5.6 Galvanic or voltaic cell : In galvanic or voltaic cells, electricity is generated through the use of spontaneous chemical reactions.

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. For example, a strip of zinc metal immersed in 1 M aqueous solution of zinc ions forms an half cell.

It follows that two metal plates and the solutions of their ions with known concentrations are required for the construction of a galvanic (voltaic) cell. Two half cells are constructed by immersing the two metal plates in solutions of their respective ions placed in separate containers. The two half cells so constructed are combined together to form the galvanic cell. The metal plates called electrodes are connected through voltmeter by a conducting wire for transfer of electrons between them. 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.

5.6.1 Salt bridge : In a galvanic cell, the two solutions are connected by a salt bridge. It is an U tube containing a saturated solution of an inert electrolyte such as KCl or NH_4NO_3 and 5 % agar solution. The ions of electrolyte do not react with the ions of electrode solutions or the electrodes.

Salt bridge is prepared by filling a U tube with hot saturated solution of the salt and agar agar solution allowing it to cool. The cooled solution sets into a gel which does not come out on inverting the tube. The salt bridge is kept dipped in distilled water when not in use as shown in Fig. 5.5.

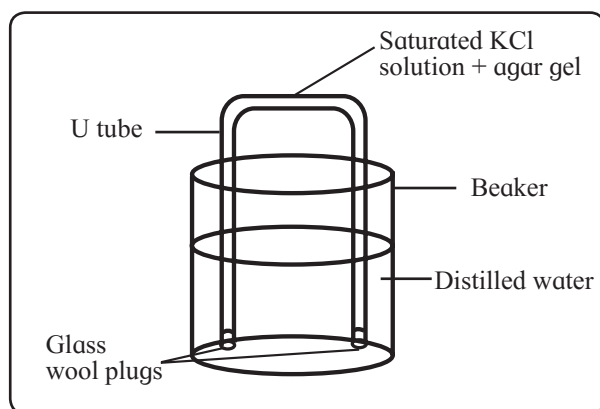
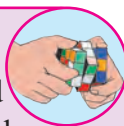


Fig. 5.5 : Salt bridge

Try this...

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.



Functions of salt bridge

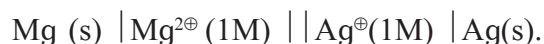
The salt bridge serves the following functions :

- It provides an electrical contact between two solutions and thereby completes the electrical circuit.
- It prevents mixing of two solutions.
- It maintains electrical neutrality in both the solutions by transfer of ions.

5.6.2 Formulation or short notation of galvanic cells : 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. The following conventions are used to write the cell notation.

- 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.
- The insoluble species if any or gases are placed in the interior position adjacent to the metal electrodes.
- The aqueous solutions of ions are placed at the middle of the cell formula.
- A single vertical line between two phases indicates the phase boundary. It indicates the direct contact between them.
- A double vertical line between two solutions indicates that they are connected by salt bridge.
- The additional information such as concentration of solutions and gas pressures is also given.
- A single half cell is written in the order: aqueous solution of ions first and then the solid electrode.

For example $\text{Zn}^{2+}(\text{1M}) \mid \text{Zn (s)}$. This order is reversed when the electrode acts as anode in the cell. The following example illustrates these conventions. The cell composed of Mg (anode) and Ag (cathode) consists of two half cells, $\text{Mg}^{2+}(\text{1M}) \mid \text{Mg (s)}$ and $\text{Ag}^{+}(\text{1M}) \mid \text{Ag(s)}$. The cell is represented as :



Can you tell ?

You have learnt Daniel cell in XI th standard. Write notations for anode and cathode. Write the cell formula.



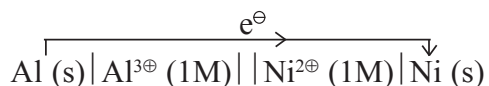
5.6.3 Writing of cell reaction : The cell reaction corresponding to the cell notation is written on the assumption that the right hand side electrode is cathode (+) and left hand side electrode is anode (-).

As mentioned in section 5.4.2, oxidation half reaction occurs at anode and reduction half reaction at cathode. It, therefore, follows that in galvanic cell oxidation half reaction takes place on the left hand side electrode and reduction half reaction on the right hand side electrode.

The following steps are followed to write the cell reaction.

- Write oxidation half reaction for the left hand side electrode (anode) and reduction half reaction for the right hand side electrode, (cathode).
- Add two electrode half reactions to get the overall cell reaction. While adding the electrons must be balanced. 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.
- 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 $2H^+(aq) + 2e^- \longrightarrow H_2(g)$ or $H^+(aq) + e^- \longrightarrow 1/2 H_2(g)$ makes no difference. In writing the overall cell reaction, the electrons must be balanced.

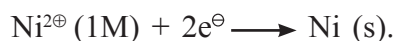
Consider the cell,



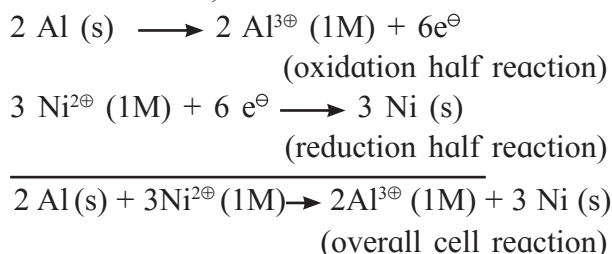
The oxidation at anode is



The reduction half reaction at cathode is

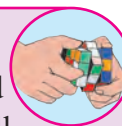


To balance the electrons, oxidation reaction is multiplied by 2 and reduction reaction by 3. The two half reactions so obtained when added give the overall cell reaction. Thus,



Try this...

Write electrode reactions and overall cell reaction for Daniel cell you learnt in standard XI.



5.7 Electrode potential and cell potential

: A galvanic cell is composed of two half cells, each consisting of electronic (metal plates) and electrolytic (solution of ions) conductors in contact. At the surface of separation of solid metal and the solution, there exists difference of electrical potential. This **potential difference established due to electrode half reaction occurring at the electrode surface, is the electrode potential.**

The potential is associated with each of the half reaction, be it oxidation or reduction. The potential associated with oxidation reaction is oxidation potential while that associated with reduction gives the reduction potential. The overall cell potential, also called electromotive force (emf), is made of the contributions from each of the electrodes. In other words, the cell potential is algebraic sum of the electrode potentials,

$$E_{cell} = E_{oxi}(\text{anode}) + E_{red}(\text{cathode}) \quad \dots\dots\dots (5.22)$$

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

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.

5.7.1 Standard potentials : The electrode potential and the cell potential depend on concentrations of solutions, pressures of gases and the temperature. To facilitate comparison of different galvanic cells, it is necessary to measure the cell voltage under given set of standard conditions of concentration and temperature.

The standard conditions chosen are 1 M concentration of solution, 1 atm pressure for gases, solids and liquids in pure form and 25°C. The voltage measured under these conditions is called standard potential designated as E^0 .

The standard cell potential is the algebraic sum of the standard electrode potentials similar to Eq. (5.22).

$$E_{cell}^0 = E_{oxi}^0 (\text{anode}) + E_{red}^0 (\text{cathode}) \quad \dots\dots\dots (5.23)$$

Here E_{oxi}^0 is standard oxidation potential and E_{red}^0 is the standard reduction potential.

According to IUPAC convention, standard potential of an electrode is taken as the standard reduction potential.

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 $\text{Zn}^{2+} (1\text{M}) | \text{Zn}$ 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.

It follows that the standard cell potential (emf) is written in terms of the standard potentials of the electrodes. In Eq. (5.23), $E_{oxi}^0 (\text{anode})$ is replaced by $- E_{red}^0 (\text{anode})$. We then write,

$$E_{cell}^0 = - E_{red}^0 (\text{anode}) + E_{red}^0 (\text{cathode})$$

Omitting the subscript _{red}, we have

$$E_{cell}^0 = E^0 (\text{cathode, +}) - E^0 (\text{anode, -}) \quad \dots\dots\dots (5.24)$$

Remember...

- While constructing a galvanic cell from two electrodes, the electrode with higher standard potential is cathode (+) and that with lower standard potential is anode (-).
- The difference in electrical potential between anode and cathode is cell voltage.



5.7.2 Dependence of cell potential on concentration (Nernst equation) :

The standard cell potential tells us whether or not the reactants in their standard states form the products in their standard states spontaneously. To predict the spontaneity of reactions for anything other than standard concentration conditions we need to know how voltage of galvanic cell varies with concentration.

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



The cell voltage is given by

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

$$= E_{cell}^0 - \frac{2.303RT}{nF} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots\dots\dots (5.25)$$

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

$$\text{At } 25^\circ\text{C}, \frac{2.303RT}{F} = 0.0592 \text{ V}$$

Therefore at 25°C , eq. (5.24) becomes

$$E_{cell} = E_{cell}^0 - \frac{0.0592\text{V}}{n} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots\dots\dots (5.26)$$

The Eq. (5.25) or Eq. (5.26) is the Nernst equation. The first term on the right hand of Nernst equation represents standard state electrochemical conditions. The second term is the correction for non standard state conditions. The cell potential equals standard potential if the concentrations of reactants and products are 1 M each. Thus,

if $[A] = [B] = [C] = [D] = 1M$,

$$E_{cell} = E_{cell}^0$$

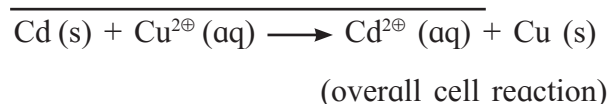
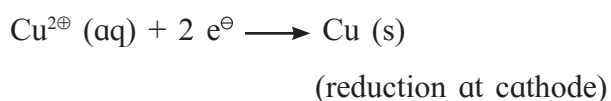
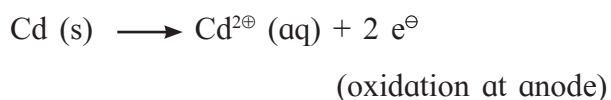
If a gaseous substance is present in the cell reaction its concentration term is replaced by the partial pressure of the gas.

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

i. Calculation of cell potential : Consider the cell



Let us first write the cell reaction



Here $n = 2$

The potential of cell is given by Nernst equation,

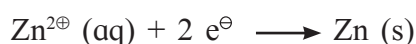
$$E_{cell} = E_{cell}^0 - \frac{0.0592}{2} \log_{10} \frac{[Cd^{2+}]}{[Cu^{2+}]} \quad \text{at } 25^\circ C.$$

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

ii. Calculation of electrode potential

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

The reduction reaction for the electrode is



Applying Nernst equation, electrode potential is given by

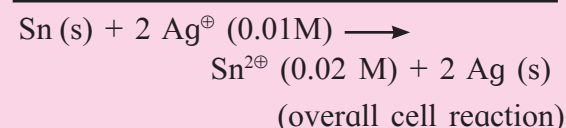
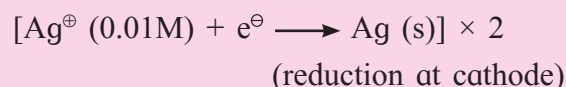
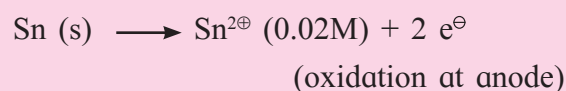
$$\begin{aligned} E_{Zn} &= E_{Zn}^0 - \frac{0.0592}{2} \log_{10} \frac{1}{[Zn^{2+}]} \\ &= E_{Zn}^0 + \frac{0.0592}{2} \log_{10} [Zn^{2+}] \quad \text{at } 25^\circ C \end{aligned}$$

Problem 5.10 : Calculate the voltage of the cell, $Sn(s) | Sn^{2+}(0.02M) || Ag^+(0.01M) | Ag(s)$ at $25^\circ C$.

$$E_{Sn}^0 = -0.136 V, \quad E_{Ag}^0 = 0.800 V.$$

Solution :

First we write the cell reaction.



The cell potential is given by

$$\begin{aligned} E_{cell} &= E_{cell}^0 - \frac{0.0592V}{2} \log_{10} \frac{[Sn^{2+}]}{[Ag^+]^2} \\ E_{cell}^0 &= E_{Ag}^0 - E_{Sn}^0 = 0.8V + 0.136V \\ &= 0.936V \end{aligned}$$

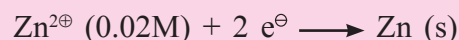
Hence,

$$\begin{aligned} E_{cell} &= 0.936V - \frac{0.0592V}{2} \log_{10} \frac{0.02}{(0.01)^2} \\ &= 0.936V - \frac{0.0592V}{2} \log_{10} 200 \\ &= 0.936V - \frac{0.0592V}{2} \times 2.301 \\ &= 0.936V - 0.0681V = 0.8679V \end{aligned}$$

Problem 5.11 : The standard potential of the electrode, $Zn^{2+}(0.02M) | Zn(s)$ is $-0.76V$. Calculate its potential.

Solution :

Electrode reaction :



$$\begin{aligned} E_{Zn} &= E_{Zn}^0 - \frac{0.0592V}{n} \log_{10} \frac{1}{[Zn^{2+}]} \\ &= -0.76V + \frac{0.0592V}{2} \log_{10} (0.02) \\ &= -0.76V + \frac{0.0592V}{2} \times (-1.6990) \\ &= -0.76V - 0.0503V = -0.81V \end{aligned}$$

5.8 Thermodynamics of galvanic cells

5.8.1 Gibbs energy of cell reactions and cell potential : The electrical work done in a galvanic cell is the electricity (charge) passed multiplied by the cell potential.

Electrical work

= amount of charge passed $\times$ cell potential.

Charge of one mole electrons is F coulombs. For the cell reaction involving n moles of electrons.

charge passed = nF coulombs

Hence, electrical work = nFE_{cell}

W. Gibbs in 1878 concluded that electrical work done in galvanic cell is equal to the decrease in Gibbs energy, $-\Delta G$, of cell reaction. It then follows that

Electrical work = $-\Delta G$

and thus $-\Delta G = nFE_{cell}$

or $\Delta G = -nFE_{cell}$ (5.27)

Under standard state conditions, we write

$$\Delta G^0 = -nFE_{cell}^0 \quad \text{..... (5.28)}$$

The Eq. (5.28) explains why E_{cell}^0 is an intensive property.

We know that ΔG^0 is an extensive property since its value depends on the amount of substance. 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. The moles of electrons transferred also doubles. The ratio,

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

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

Thus, E_{cell}^0 remains the same by multiplying the redox reaction by 2. It means E_{cell}^0 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.

5.8.2 Standard cell potential and equilibrium constant : The relation between standard Gibbs energy change of cell reaction and standard cell potential is given by Eq. (5.27).

$$-\Delta G^0 = nFE_{cell}^0$$

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

$$\Delta G^0 = -RT \ln K \quad \text{..... (5.29)}$$

Combining Eq. (5.28) and Eq. (5.29), we have

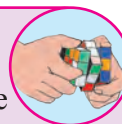
$$-nFE_{cell}^0 = -RT \ln K$$

$$\text{or } E_{cell}^0 = \frac{RT}{nF} \ln K$$

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

$$= \frac{0.0592}{n} \log_{10} K \quad \text{at } 25^\circ\text{C} \quad \text{..... (5.29)}$$

Try this...



Write expressions to calculate equilibrium constant from

- Concentration data
- Thermochemical data
- Electrochemical data

Problem 5.12 : Calculate standard Gibbs energy change and equilibrium constant at 25°C for the cell reaction,



Given : $E_{\text{Cd}}^0 = -0.403\text{V}$ and $E_{\text{Sn}}^0 = -0.136\text{V}$. Write formula of the cell.

Solution :

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

ii. $\Delta G^0 = -nF E_{\text{cell}}^0$

$$E_{\text{cell}}^0 = E_{\text{Sn}}^0 - E_{\text{Cd}}^0 = -0.136\text{V} - (-0.403\text{V}) \\ = 0.267\text{V}.$$

$$n = 2 \text{ mol e}^-$$

$$\Delta G^0 = -2 \text{ mol e}^- \times 96500 \text{ C/mol e}^- \times 0.267\text{V} \\ = -51531 \text{ V C} = -51531 \text{ J} = -51.53 \text{ kJ}$$

iii. $E_{\text{cell}}^0 = \frac{0.0592\text{V}}{2} \log_{10} K$

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

$$\log_{10} K = \frac{0.267 \times 2}{0.0592} = 9.0203$$

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

5.9 Reference electrodes : Every oxidation needs to be accompanied by reduction. The occurrence of only oxidation or only reduction is not possible. (Refer to Std. XI Chemistry Textbook Chapter 6)

In a galvanic cell oxidation and reduction occur simultaneously. The potential associated with the redox reaction can be experimentally measured. For the measurement of potential two electrodes need to be combined together where the redox reaction occurs.

What would happen if potential of one of the electrodes in a galvanic cell is zero ? Can we measure the potential of such a galvanic cell ? There are two electrodes combined together and a redox reaction results. The measured cell potential is algebraic sum of two electrode potentials. One electrode potential is zero. Therefore, the measured cell potential is equal to the potential of other electrode.

From foregoing arguments, it follows that it is necessary to choose an arbitrary standard electrode as a reference point. 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. The potential of this electrode has arbitrarily been taken as zero. The electrode is called standard hydrogen electrode (SHE).

We will see later that SHE is not the most convenient electrode. Several other electrodes namely calomel, silver-silver chloride and glass electrodes with known potentials are used as secondary reference electrodes. The potentials of these electrodes are determined using SHE.

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

5.9.1 Standard hydrogen electrode (SHE) :

Construction : SHE consists of a platinum plate, coated with platinum black used as electrodes. This plate is connected to the external circuit through sealed narrow glass tube containing mercury. It is surrounded by an outer jacket.

The platinum electrode is immersed in 1 M H^+ ion solution. 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 Fig.5.6. Platinum does not take part in the electrode reaction. It is inert electrode and serves as the site for electron transfer.

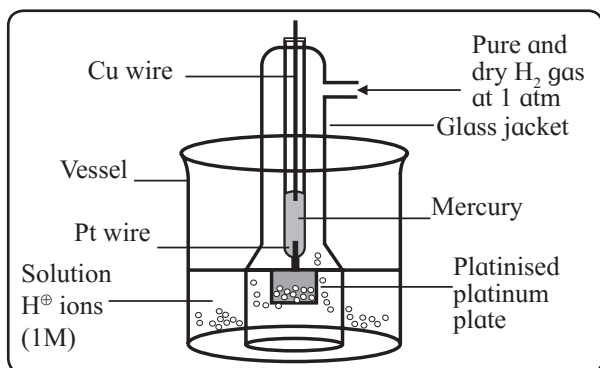


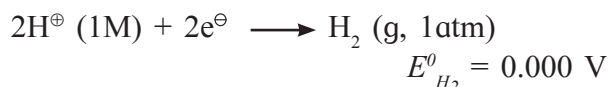
Fig. 5.6 : Standard hydrogen electrode

Formulation : Standard hydrogen electrode is represented as



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.

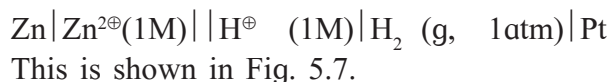
The reduction half reaction at the electrode is



Application of SHE

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

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



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

$$E^0_{\text{cell}} = E^0_{\text{H}_2} - E^0_{\text{Zn}} = -E^0_{\text{Zn}}, \text{ because } E^0_{\text{H}_2} \text{ is zero.}$$

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

Difficulties in setting SHE

- It is difficult to obtain pure and dry hydrogen gas.
- The pressure of hydrogen gas cannot be maintained exactly at 1 atm throughout the measurement.

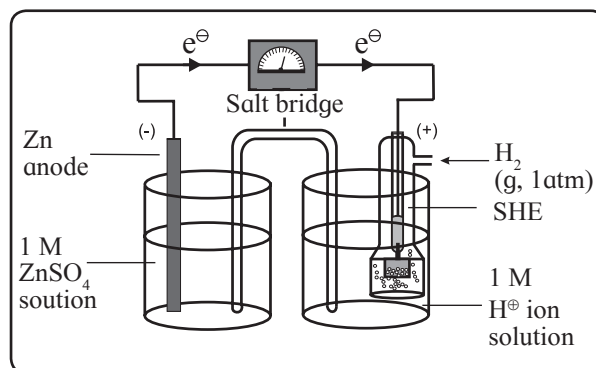


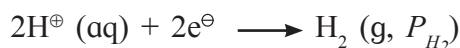
Fig. 5.7 : Determination of standard potential using SHE

- 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.

Hydrogen gas electrode

For hydrogen gas electrode, $\text{H}^+(\text{aq}) | \text{H}_2(\text{g}, P_{\text{H}_2}) | \text{Pt}$, $[\text{H}^+]$ and pressure of hydrogen gas differ from unity.

Electrode reaction :



From the Nernst equation

$$E_{\text{H}_2} = E^0_{\text{H}_2} - \frac{0.0592}{2} \log_{10} \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$= - \frac{0.0592}{2} \log_{10} \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

Because $E^0_{\text{H}_2} = 0$

5.10 Galvanic cells useful in day-to-day life

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

- Primary voltaic cells :** When a galvanic cell discharges during current generation, the chemicals are consumed. In primary voltaic cell, once the chemicals are completely consumed, cell reaction stops. The cell reaction cannot be reversed even after reversing the direction of current flow or these cells cannot be recharged. The most familiar example is dry cell.

ii. Secondary voltaic cells : In secondary voltaic cell, the chemicals consumed during current generation can be regenerated. For this purpose an external potential slightly greater than the cell potential is applied across the electrodes. This results in reversal of the direction of current flow causing the reversal of cell reaction. This is recharging of cell. The voltaic cells which can be recharged are called secondary voltaic cells.

It is amazing to see that 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.

5.10.1 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 prevent drying of the paste by evaporation of moisture. See Fig. 5.8.

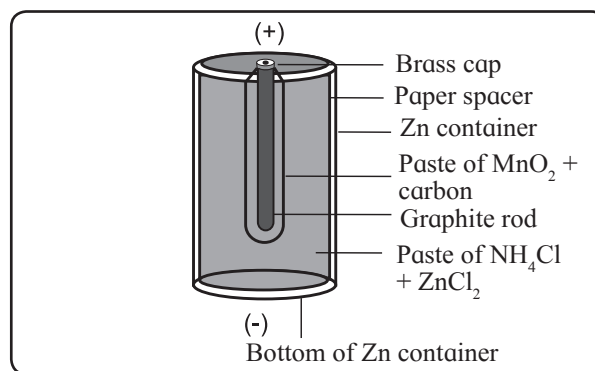


Fig. 5.8 : Dry cell (Leclanche' cell)

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.



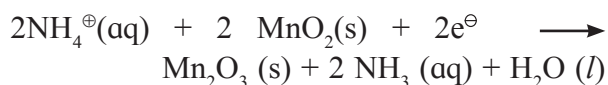
ii. Reduction at cathode : The electrons liberated in oxidation at anode flow along the container and migrate to cathode. At cathode NH_4^{+} ions are reduced.



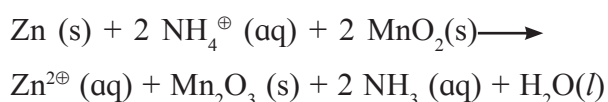
Hydrogen gas produced in reduction reaction is oxidised by MnO_2 and prevents its collection on cathode.



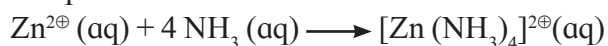
The net reduction reaction at cathode is combination of these two reactions.



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



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



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.

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

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

Construction : 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 (+).

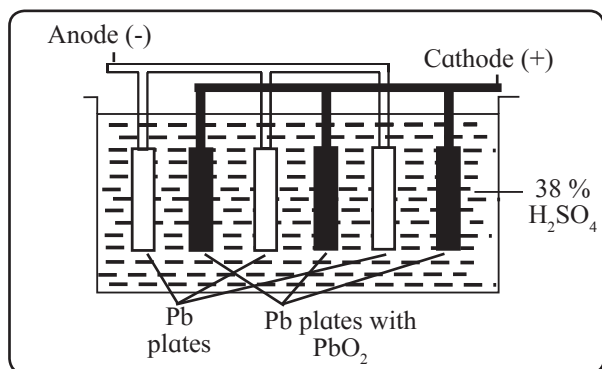


Fig. 5.9 : Lead storage cell

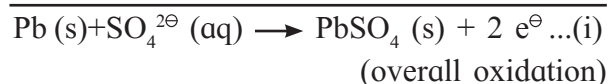
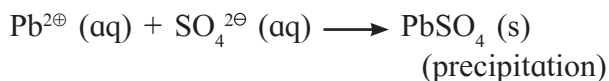
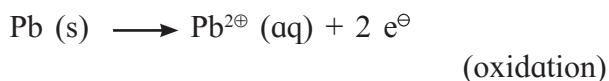
To provide large reacting surface, the cell contains several plates of each type. The two types of plates are alternately arranged as shown in Fig. 5.9.

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

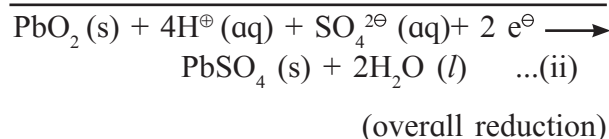
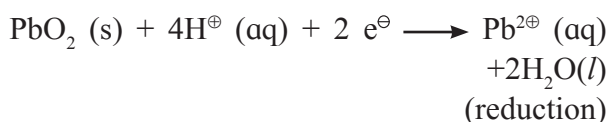
Notation of the cell : The cell is formulated as $\text{Pb(s)} | \text{PbSO}_4(\text{s}) | 38\% \text{H}_2\text{SO}_4(\text{aq}) | \text{PbSO}_4(\text{s}) | \text{PbO}_2(\text{s}) | \text{Pb(s)}$

a. Cell reactions during discharge

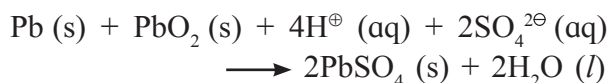
i. **Oxidation at anode (-) :** When the cell provides current, spongy lead is oxidised to Pb^{2+} ions and negative charge accumulates on lead plates. The Pb^{2+} ions so formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble PbSO_4 . The net oxidation is the sum of these two processes.



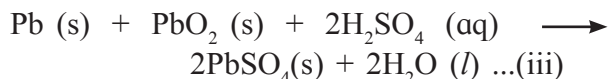
ii. **Reduction at cathode (+) :** The electrons produced at anode travel through external circuit and re-enter the cell at cathode. At cathode PbO_2 is reduced to Pb^{2+} ions in presence of H^+ ions. Subsequently Pb^{2+} ions so formed combine with SO_4^{2-} ions from H_2SO_4 to form insoluble PbSO_4 that gets coated on the electrode.



iii. **Net cell reaction during discharge:** The net cell reaction is the sum of overall oxidation at anode and overall reduction at cathode.



or



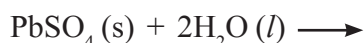
As the cell operates to generate current, H_2SO_4 is consumed. Its concentration (density) decreases and the cell potential is decreased. The cell potential thus depends on sulphuric acid concentration (density).

b. Cell reactions during recharging :

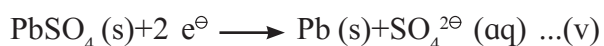
The potential of lead accumulator is 2V. It must be recharged with the falling of the cell potential to 1.8 V. To recharge the cell external potential slightly greater than 2 V needs to be applied across the electrodes.

During recharging the cell functions as electrolytic cell. The anode and cathode are interchanged with PbO_2 electrode being anode (+) and lead electrode cathode (-).

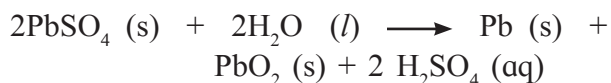
iv. Oxidation at anode (+) : It is reverse of reduction reaction (ii) at cathode that occurs during discharge.



v. Reduction at cathode (-) : It is reverse of oxidation reaction (i) at anode that occurs during discharge.



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



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

Applications of lead accumulator

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

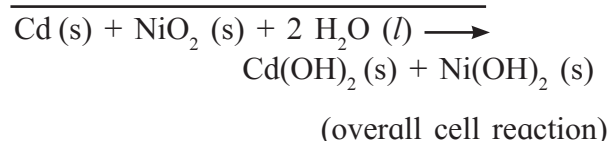
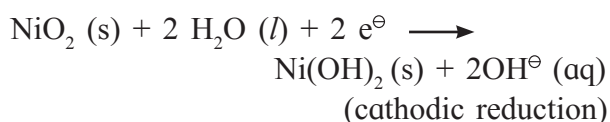
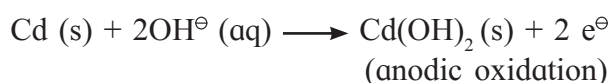
ii. A 12 V lead storage battery constructed by connecting six 2 V cells in series is used in automobiles and inverters.

5.10.3 Nickel-Cadmium or NICAD storage cell :

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

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.

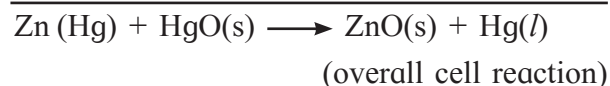
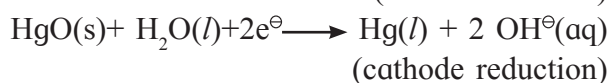
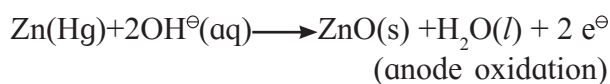
The electrode reactions and overall cell reaction are as follows :



The reaction product at each electrode is solid that adheres to electrode surface. Therefore the cell can be recharged. The potential of the cell is about 1.4 V. The cell has longer life than other dry cells. It can be used in electronic watches, calculators, photographic equipments, etc.

5.10.4 Mercury battery :

Mercury battery is a secondary dry cell and can be recharged. The mercury battery consists of zinc anode, amalgamated with mercury. The cathode is a paste of Hg and carbon. The electrolyte is strongly alkaline and made of a paste of KOH and ZnO. The electrode reactions and net cell reaction are :



The overall reaction involves only solid substances. There is no change in electrolyte composition during operation. The mercury battery, therefore, provides more constant voltage (1.35V) than the Leclanche' dry cell. It also has considerably higher capacity and longer life than dry cell.

The mercury dry cell finds use in hearing aids, electric watches, pacemakers, etc.

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

The fuel cells differ from ordinary galvanic cells in that the reactants are not placed within the cell. They are continuously supplied to electrodes from a reservoir.

In these cells one of the reactants is a fuel such as hydrogen gas or methanol. The other reactant such as oxygen, is oxidant.

The simplest fuel cell is hydrogen-oxygen fuel cell.

5.11.1 Hydrogen-oxygen fuel cell : In $H_2 - O_2$ fuel cell, the fuel is hydrogen gas. Oxygen gas is an oxidising agent. The energy of the combustion of hydrogen is converted into electrical energy.

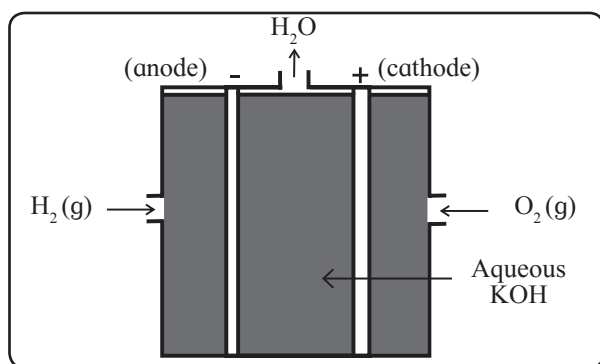


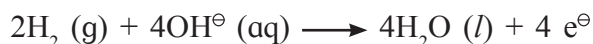
Fig. 5.10 : $H_2 - O_2$ fuel cell

Construction : The anode and cathode are porous carbon rods containing small amount of finely divided platinum metal that acts as a catalyst. The electrolyte is hot aqueous solution of KOH. The carbon rods immersed into electrolyte are shown in Fig. 5.10.

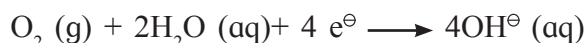
Hydrogen gas is continuously bubbled, through anode and oxygen gas through cathode into the electrolyte.

Cell reactions

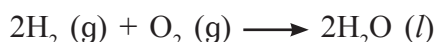
i. Oxidation at anode (-) : At anode hydrogen gas is oxidised to H_2O .



ii. Reduction at cathode (+) : The electrons released at anode travel, through external circuit to cathode. Here O_2 is reduced to OH^- .



iii. Net cell reaction : The overall cell reaction is the sum of electrode reactions (i) and (ii).



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.

The chemical energy released during the formation of O-H bond is directly converted into electrical energy accompanying in above combustion reaction. The cell continues to operate as long as H_2 and O_2 gases are supplied to electrodes.

The cell potential is given by

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0 = 0.4V - (-0.83V) = 1.23 V.$$

Advantages of fuel cells

- 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.
- They are nonpolluting as the only reaction product is water.
- Fuel cells provide electricity with an efficiency of about 70 % which is twice as large when compared with efficiency of thermal plants (only 40 %).

Drawbacks of fuel cell

H₂ gas is hazardous to handle and the cost of preparing H₂ is high.

Internet my friend

Fuel cells are also used in cell phones and laptop computers. The cell proposed for use in these products is direct methanol fuel cell (DMFC). Collect information of this cell.



Applications of fuel cells

- The fuel cells are used on experimental basis in automobiles.
- The fuel cell are used for electrical power in the space programme.
- 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.
- In future, fuel cells can possibly be explored as power generators in hospitals, hotels and homes.

Can you tell ?

In what ways are fuel cells and galvanic cells similar and in what ways are they different ?



5.12 Electrochemical series (Electromotive series) : 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 as shown in Table 5.1. This arrangement is called electrochemical series.

Key points of electrochemical series

- 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.

- Below hydrogen electrode the negative standard potential increases and above hydrogen electrode the positive standard potential increases.
- E^0 values apply to the reduction half reactions that occur in the forward direction as written.
- Higher (more positive) E^0 value 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.

The half reactions are listed in order of their decreasing tendency in the forward direction.

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).



Applications of electrochemical series

- Relative strength of oxidising agents:** 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. 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. 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.

Use your brain power

Identify the strongest and the weakest oxidizing agents from the electrochemical series.



ii. Relative strength of reducing agents:

The species on the right side of half reactions are reducing agents.

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. 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. They serve as strong reducing agents. The strength of reducing agents increases from top to bottom as E^0 values decrease.

Use your brain power

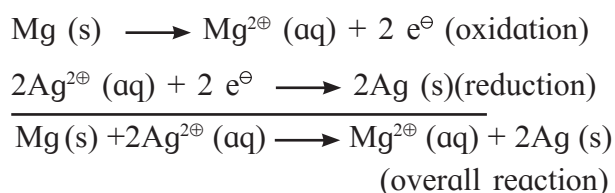
Identify the strongest and the weakest reducing agents from the electrochemical series.



iii. Spontaneity of redox reactions : 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).

The standard cell potential must be positive for a cell reaction to be spontaneous under the standard conditions. Noteworthy application of electromotive series is predicting spontaneity of redox reactions from the knowledge of standard potentials.

Suppose, we ask a question : At standard conditions would $\text{Ag}^{\oplus}$ ions oxidise metallic magnesium ? To answer this question, first we write oxidation of Mg by $\text{Ag}^{\oplus}$.



From Table 5.1 of electrochemical series we have

$E^0_{\text{Mg}} = -2.37 \text{ V}$ and $E^0_{\text{Ag}} = 0.8 \text{ V}$. For the cell having Mg as anode and Ag cathode.

$$\begin{aligned} E^0_{\text{Cell}} &= E^0_{\text{Ag}} - E^0_{\text{Mg}} = 0.8\text{V} - (-2.37\text{V}) \\ &= 3.17 \text{ V.} \end{aligned}$$

EMF being positive the cell reaction is spontaneous. Thus $\text{Ag}^{\oplus}$ ions oxidise to metallic Mg.

General rules

- An oxidizing agent can oxidize any reducing agent that appears below it, and cannot oxidize the reducing agent appearing above it in the electrochemical series.
- An reducing agent can reduce the oxidising agent located above it in the electrochemical series.

Use your brain power

From E^0 values given in Table 5.1, predict whether Sn can reduce I_2 or $\text{Ni}^{2\oplus}$.



Do you know ?

The fuel cells for power electric vehicles incorporate the proton conducting plastic membrane. These are proton exchange membranes (PEM) fuel cells.



**Table 5.1 : The standard aqueous electrode potentials at 298 K
(Electrochemical series)**

Electrode	Half reaction		E° V
	Left side species (oxidizing agents)	Right side species (Reducing agents)	
$F^{\ominus} F_2 Pt$	$\uparrow$	$F_2 + 2 e^{\ominus} \longrightarrow F^{\ominus}$	+2.870
$Au^{\oplus} Au$		$Au^{\oplus} + e^{\ominus} \longrightarrow Au$	+1.680
$Ce^{4\oplus}, Ce^{3\oplus} Pt$		$Ce^{4\oplus} + e^{\ominus} \longrightarrow Ce^{3\oplus}$	+1.610
$Au^{3\oplus} Au$		$Au^{3\oplus} + 3e^{\ominus} \longrightarrow Au$	+1.500
$Cl^{\ominus} Cl_2 Pt$		$Cl_2 + 2e^{\ominus} \longrightarrow 2Cl^{\ominus}$	+1.360
$Pt^{2\oplus} Pt$		$Pt^{2\oplus} + 2e^{\ominus} \longrightarrow Pt$	+1.200
$Br^{\ominus} Br_2 Pt$		$Br_2 + 2e^{\ominus} \longrightarrow 2Br^{\ominus}$	+1.080
$Hg^{2\oplus} Hg$		$Hg^{2\oplus} + 2e^{\ominus} \longrightarrow Hg$	+0.854
$Ag^{\oplus} Ag$	Increasing strength as oxidising agent	$Ag^{\oplus} + e^{\ominus} \longrightarrow Ag$	+0.799
$Hg_2^{2\oplus} Hg$		$Hg_2^{2\oplus} + 2e^{\ominus} \longrightarrow 2Hg$	+0.79
$Fe^{3\oplus}, Fe^{2\oplus} Pt$		$Fe^{3\oplus} + e^{\ominus} \longrightarrow Fe^{2\oplus}$	+0.771
$I^{\ominus} I_2(s) Pt$		$I_2 + 2e^{\ominus} \longrightarrow 2I^{\ominus}$	+0.535
$Cu^{2\oplus} Cu$		$Cu^{2\oplus} + 2e^{\ominus} \longrightarrow Cu$	+0.337
$Ag AgCl(s) Cl^{\ominus}$		$AgCl(s) + e^{\ominus} \longrightarrow Ag + Cl^{\ominus}$	+0.222
$Cu^{2\oplus}, Cu^{\oplus} Pt$		$Cu^{2\oplus} + e^{\ominus} \longrightarrow Cu^{\oplus}$	+0.153
$Sn^{4\oplus}, Sn^{2\oplus} Pt$		$Sn^{4\oplus} + 2e^{\ominus} \longrightarrow Sn^{2\oplus}$	+0.15
$H^{\oplus} H_2 Pt$		$2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$	0.00
$Pb^{2\oplus} Pb$		$Pb^{2\oplus} + 2e^{\ominus} \longrightarrow Pb$	-0.126
$Sn^{2\oplus} Sn$		$Sn^{2\oplus} + 2e^{\ominus} \longrightarrow Sn$	-0.136
$Ni^{2\oplus} Ni$		$Ni^{2\oplus} + 2e^{\ominus} \longrightarrow Ni$	-0.257
$Co^{2\oplus} Co$		$Co^{2\oplus} + 2e^{\ominus} \longrightarrow Co$	-0.280
$Cd^{2\oplus} Cd$		$Cd^{2\oplus} + 2e^{\ominus} \longrightarrow Cd$	-0.403
$Fe^{2\oplus} Fe$		$Fe^{2\oplus} + 2e^{\ominus} \longrightarrow Fe$	-0.440
$Cr^{3\oplus} Cr$		$Cr^{3\oplus} + 3e^{\ominus} \longrightarrow Cr$	-0.740
$Zn^{2\oplus} Zn$		$Zn^{2\oplus} + 2e^{\ominus} \longrightarrow Zn$	-0.763
$Al^{3\oplus} Al$		$Al^{3\oplus} + 3e^{\ominus} \longrightarrow Al$	-1.66
$Mg^{2\oplus} Mg$		$Mg^{2\oplus} + 2e^{\ominus} \longrightarrow Mg$	-2.37
$Na^{\oplus} Na$		$Na^{\oplus} + e^{\ominus} \longrightarrow Na$	-2.714
$Ca^{2\oplus} Ca$		$Ca^{2\oplus} + 2e^{\ominus} \longrightarrow Ca$	-2.866
$K^{\oplus} K$		$K^{\oplus} + e^{\ominus} \longrightarrow K$	-2.925
$Li^{\oplus} Li$		$Li^{\oplus} + e^{\ominus} \longrightarrow Li$	-3.045

Note : (i) all ions are at 1 M concentration in water.

(ii) all gases are at 1 atm pressure.

Exercises

1. Choose the most correct option.

- i. Two solutions have the ratio of their concentrations 0.4 and ratio of their conductivities 0.216. The ratio of their molar conductivities will be

a. 0.54 b. 11.574
c. 0.0864 d. 1.852

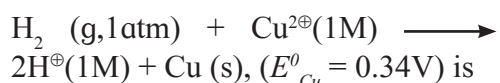
- ii. On diluting the solution of an electrolyte

a. both $\wedge$ and k increase
b. both $\wedge$ and k decrease
c. $\wedge$ increases and k decreases
d. $\wedge$ decreases and k increases

- iii. $1 \text{ S m}^2 \text{ mol}^{-1}$ is equal to

a. $10^{-4} \text{ S m}^2 \text{ mol}^{-1}$
b. $10^4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
c. $10^{-2} \text{ S cm}^2 \text{ mol}^{-1}$
d. $10^2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$

- iv. The standard potential of the cell in which the following reaction occurs

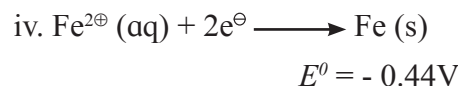
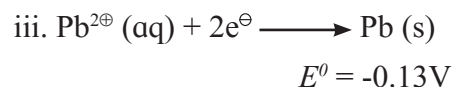
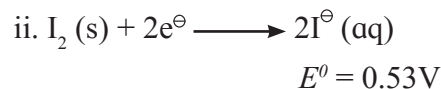
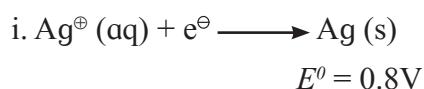


a. -0.34 V b. 0.34 V
c. 0.17 V d. -0.17 V

- v. For the cell, $\text{Pb} (\text{s}) | \text{Pb}^{2+}(\text{1M}) || \text{Ag}^+(\text{1M}) | \text{Ag} (\text{s})$, if concentration of an ion in the anode compartment is increased by a factor of 10, the emf of the cell will

a. increase by 10 V
b. increase by 0.0296 V
c. decrease by 10 V
d. decrease by 0.0296 V

- vi. Consider the half reactions with standard potentials



The strongest oxidising and reducing agents respectively are

a. Ag and Fe^{2+} b. Ag^+ and Fe
c. Pb^{2+} and I^- d. I_2 and Fe^{2+}

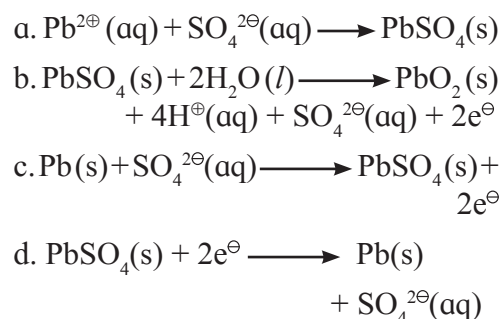
- vii. For the reaction $\text{Ni}(\text{s}) + \text{Cu}^{2+} (\text{1M}) \longrightarrow \text{Ni}^{2+} (\text{1M}) + \text{Cu} (\text{s})$, $E^0_{\text{cell}} = 0.57\text{V}$ ΔG^0 of the reaction is

a. 110 kJ b. -110 kJ
c. 55 kJ d. -55 kJ

- viii. Which of the following is not correct?

a. Gibbs energy is an extensive property
b. Electrode potential or cell potential is an intensive property.
c. Electrical work = - ΔG
d. If half reaction is multiplied by a numerical factor, the corresponding E^0 value is also multiplied by the same factor.

- ix. The oxidation reaction that takes place in lead storage battery during discharge is



- x. Which of the following expressions represent molar conductivity of $\text{Al}_2(\text{SO}_4)_3$?

- $3 \lambda_{\text{Al}^{3+}}^0 + 2 \lambda_{\text{SO}_4^{2-}}^0$
- $2 \lambda_{\text{Al}^{3+}}^0 + 3 \lambda_{\text{SO}_4^{2-}}^0$
- $1/3 \lambda_{\text{Al}^{3+}}^0 + 1/2 \lambda_{\text{SO}_4^{2-}}^0$
- $\lambda_{\text{Al}^{3+}}^0 + \lambda_{\text{SO}_4^{2-}}^0$

2. Answer the following in one or two sentences.

- What is a cell constant?
- Write the relationship between conductivity and molar conductivity and hence unit of molar conductivity.
- Write the electrode reactions during electrolysis of molten KCl.
- Write any two functions of salt bridge.
- What is standard cell potential for the reaction
 $2\text{Al(s)} + 3\text{Ni}^{2+}(\text{1M}) \longrightarrow 2\text{Al}^{3+}(\text{1M}) + 3\text{Ni(s)}$
 if $E_{\text{Ni}}^0 = -0.25 \text{ V}$ and $E_{\text{Al}}^0 = -1.66 \text{ V}$?
- Write Nernst equation. What part of it represents the correction factor for nonstandard state conditions?
- Under what conditions the cell potential is called standard cell potential?
- Formulate a cell from the following electrode reactions :
 $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au(s)}$
 $\text{Mg(s)} \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$
- How many electrons would have a total charge of 1 coulomb?
- What is the significance of the single vertical line and double vertical line in the formulation galvanic cell.

3. Answer the following in brief

- Explain the effect of dilution of solution on conductivity?

- What is a salt bridge?
- Write electrode reactions for the electrolysis of aqueous NaCl.
- How many moles of electrons are passed when 0.8 ampere current is passed for 1 hour through molten CaCl_2 ?
- Construct a galvanic cell from the electrodes $\text{Co}^{3+}|\text{Co}$ and $\text{Mn}^{2+}|\text{Mn}$. $E_{\text{Co}}^0 = 1.82 \text{ V}$, $E_{\text{Mn}}^0 = -1.18 \text{ V}$. Calculate E_{cell}^0 .
- Using the relationship between ΔG^0 of cell reaction and the standard potential associated with it, how will you show that the electrical potential is an intensive property?
- Derive the relationship between standard cell potential and equilibrium constant of cell reaction.
- It is impossible to measure the potential of a single electrode. Comment.
- Why do the cell potential of lead accumulators decrease when it generates electricity? How the cell potential can be increased?
- Write the electrode reactions and net cell reaction in NICAD battery.

4. Answer the following :

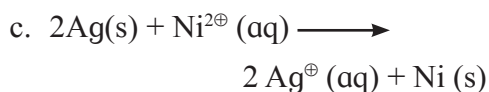
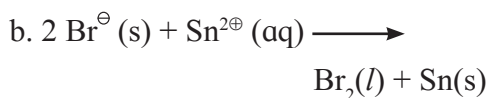
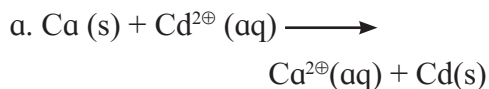
- What is Kohlrausch law of independent migration of ions? How is it useful in obtaining molar conductivity at zero concentration of a weak electrolyte? Explain with an example.
- Explain electrolysis of molten NaCl.
- What current strength in amperes will be required to produce 2.4 g of Cu from CuSO_4 solution in 1 hour? Molar mass of Cu = 63.5 g mol^{-1} . (2.03 A)
- Equilibrium constant of the reaction,
 $2\text{Cu}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu(s)}$
 is 1.2×10^6 . What is the standard

- potential of the cell in which the reaction takes place ? (0.36 V)
- v. Calculate emf of the cell
 $\text{Zn(s)} | \text{Zn}^{2+}(0.2\text{M}) || \text{H}^+(1.6\text{M}) | \text{H}_2(\text{g}, 1.8 \text{ atm}) | \text{Pt}$ at 25°C .
 (0.785V)
- vi. Calculate emf of the following cell at 25°C .
 $\text{Zn(s)} | \text{Zn}^{2+}(0.08\text{M}) || \text{Cr}^{3+}(0.1\text{M}) | \text{Cr}$
 $E^\circ_{\text{Zn}} = -0.76 \text{ V}, E^\circ_{\text{Cr}} = -0.74 \text{ V}$
 (0.0327 V)
- vii. What is a cell constant ? What are its units? How is it determined experimentally?
- viii. How will you calculate the moles of electrons passed and mass of the substance produced during electrolysis of a salt solution using reaction stoichiometry.
- ix. Write the electrode reactions when lead storage cell generates electricity. What are the anode and cathode and the electrode reactions during its recharging?
- x. What are anode and cathode of H_2 - O_2 fuel cell ? Name the electrolyte used in it. Write electrode reactions and net cell reaction taking place in the fuel cell.
- xi. What are anode and cathode for Leclanche' dry cell ? Write electrode reactions and overall cell reaction when it generates electricity.
- xii. Identify oxidising agents and arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.
 $\text{Al} (-1.66\text{V}), \text{Al}^{3+}(-1.66\text{V}), \text{Cl}_2 (1.36\text{V}), \text{Cd}^{2+}(-0.4\text{V}), \text{Fe}(-0.44\text{V}), \text{I}_2(0.54\text{V}), \text{Br}^\ominus(1.09\text{V})$.
- xiii. 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.

$\text{K} (-2.93\text{V}), \text{Br}_2(1.09\text{V}), \text{Mg}(-2.36\text{V}), \text{Ce}^{3+}(1.61\text{V}), \text{Ti}^{2+}(-0.37\text{V}), \text{Ag}^\oplus(0.8 \text{ V}), \text{Ni} (-0.23\text{V})$.

- xiv. Predict whether the following reactions would occur spontaneously under standard state conditions.



(use information of Table 5.1)

Activity :



1. Write electrode reactions net cell reaction in the electrolysis of molten barium chloride.
2. Prepare the salt bridge and set up the Daniel cell in your laboratory. Measure its emf using voltmeter and compare it with the value calculated from the information in Table 5.1
3. k_1 and k_2 are conductivities of two solutions and c_1 and c_2 are their concentrations. Establish the relationship between k_1, k_2, c_1, c_2 and molar conductivities $\wedge_1$ and $\wedge_2$ of the two solutions.
4. Find and search working of power inverters in day-to-day life.
5. Collect information of pollution free battery.