



ELECTROCHEMISTRY



- * Electrical Conductivity
- * Galvanic Cells
- * Electrolysis
- * Metallic Corrosion

ELECTRICAL CONDUCTIVITY

Electrical current flows in metals without changes occurring in metals. Solutions of acids, alkalies and salts conduct electricity, but material changes occur during conduction. Electrochemistry is mainly concerned with the relation between electrical energy and chemical energy.

4.1.1

Electrical conductors

Substance which does not allow the flow of electricity through it is called insulator. Diamond is a familiar example of insulator. Rubber, glass, plastics, etc., are other examples of insulators.

Electric current is considered in general as flow of electric charges through the conducting medium. This medium is termed as electrical conductor. Electrical conductor is defined as the substance which allows the electric current to flow through it. Electrical conductors may be solid metals, fused metals, molten salts or aqueous solutions of acids, bases and salts. Electrical conductors are broadly classified into two types.

Electronic conductors : Metals, alloys, graphite and salts like cadmium sulphide, copper sulphide, etc., are examples.

Electrolytic conductors : Fused salts and aqueous solutions of acids, alkalies, salts, etc., are examples.

The main differences between electrical conductors are listed in Table 4.1.

Table 4.1 Differences in the properties of two types of conductors

Electronic conductors	Electrolytic conductors
1. Conductivity is due to mobility of free electrons	1. Conductivity is due to mobility of free ions
2. During conduction matter is not transferred in the form of ions	2. During conduction matter is transferred in the form of ions
3. Passage of current may bring only physical changes	3. Passage of current brings in physical as well as chemical changes
4. The conductivity power is high exceptionally	4. The conductivity power is relatively less
5. An increase in temperature decreases conductivity due to increased thermal vibration of particles	5. An increase in temperature increases conductivity due to decrease in viscosity and degree of hydration of ions

Electronic conduction is also called metallic conduction. It depends upon nature, structure, density, temperature and valency of the metal. It also depends upon the composition of the alloy formed between metals.

4.1.2**Theory of electrolytes**

Fraction of total number of molecules present as ions in solution is called degree of ionisation

Electrolytic solution has ions but solution is electrically neutral

Electrolyte is defined as the substance that conducts electric current in molten or in solution state and is simultaneously decomposed. There are substances which do not conduct electricity even in the solution state. Such substances are called non-electrolytes. Cane sugar, urea, glucose, etc., are examples of non-electrolytes. In order to explain the properties of electrolytic solutions, Arrhenius proposed a theory of electrolytic dissociation which is also called ionic theory. The important points of this theory are :

1. An electrolyte in aqueous solution breaks up into two oppositely charged ions and the ions may be in equilibrium with the unionised electrolyte, $\text{BA} \rightleftharpoons \text{B}^+ + \text{A}^-$
2. The process of splitting of the electrolyte molecule into ions is called ionisation or dissociation. The fraction of total number of molecules present as ions in the solution is called degree of dissociation. It is denoted by ' α '.

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules of the electrolyte taken}}$$

3. The degree of dissociation depends upon nature of the electrolyte, nature of the solvent and temperature.
4. The equilibrium constant for the dissociation of electrolyte (K) is related to the concentration (C) as,

$$K = C\alpha^2 / (1 - \alpha)$$

5. If the extent of dissociation is high (> 0.9), the electrolytes are called strong electrolytes. Strong acids like HCl , H_2SO_4 , HNO_3 , HClO_4 , strong bases like NaOH , KOH , CsOH , $\text{Ba}(\text{OH})_2$ and highly soluble salts like NaCl , K_2SO_4 , Na_2CO_3 , KClO_4 , etc., are examples of strong electrolytes. They have high dissociation constants.
6. If the extent of dissociation is low (< 0.1), the electrolytes are called weak electrolytes. Weak bases like NH_4OH , $\text{Mg}(\text{OH})_2$ and sparingly soluble salts like AgCl , BaSO_4 , PbS , CaCO_3 , etc., are examples of weak electrolytes. They have low dissociation constants.
7. When an electric current is passed through the solution of electrolyte, the ions move towards electrodes of opposite charge and are discharged. The discharge of the ions is always in equivalent amounts, no matter what their relative speeds are.
8. The properties of electrolytes in solution are the properties of ions in the solution. Solutions rich with protons are called acidic and rich with hydroxyl ions are basic. The electrolytic solution is, however, electrically neutral.
9. The extent of dissociation of electrolyte increases with decrease in concentration. It approaches unity at infinite dilution.
10. The conductivity of electrolytic solution depends on the degree of dissociation and the number of ions, as the electric current is carried through the movement of ions in the solution.

4.1.3**Conductance**

Like metals, electrolytic solutions also conduct electricity. The solutions of electrolytes too obey Ohm's law. These solutions also offer resistance to the flow of electric current.

A conductivity cell is shown in Fig 4.1. The resistance 'R' to the flow of current offered by the solution of electrolyte in the cell is inversely proportional to the area of cross section (a) of the electrode and is directly proportional to the distance of separation (l).


Unit of cell
constant is m^{-1}


Resistance offered by the solution, $R \propto \frac{l}{a}$ (or) $R = \rho \frac{l}{a}$

Here, ρ is the specific resistance, also called resistivity. The ratio of length (l) and area of cross section (a) is called cell constant. Unit of cell constant is cm^{-1} or m^{-1} .

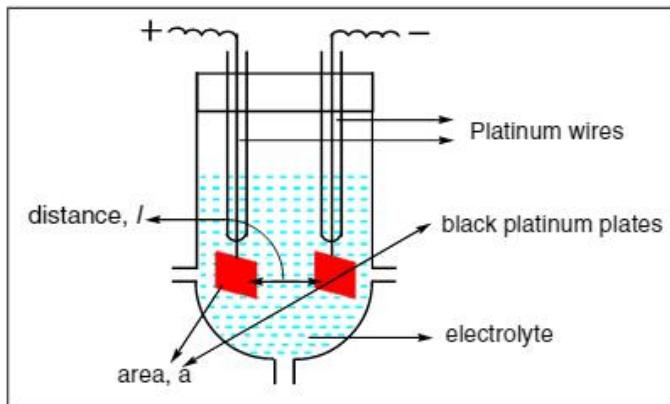


Fig 4.1 Commonly used Conductivity cell

The reciprocal of resistance is known as conductance (C).

$$C = \frac{1}{R} = \frac{1}{\rho} \times \frac{1}{l/a} \quad (\text{or}) \quad C = k \frac{1}{(l/a)} \quad (\text{or}) \quad k = C \times \frac{l}{a}$$

Here k is specific conductance, also called conductivity. It is the reciprocal of specific resistance. Resistance is expressed in ohm. The symbol of ohm is ' Ω '. Conductance is expressed in ohm^{-1} or mho. In SI system ohm^{-1} is Siemen. The symbol of Siemen is 'S'. Units of specific conductance are $ohm^{-1}cm^{-1}$ in CGS system and $S\ m^{-1}$ in SI system. Specific conductance is the conductance of the electrolyte in unit volume of the solution. Conductance and specific conductance are one and the same if cell constant is unity.

Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. The set up for the measurement of the resistance is shown in Fig 4.2.

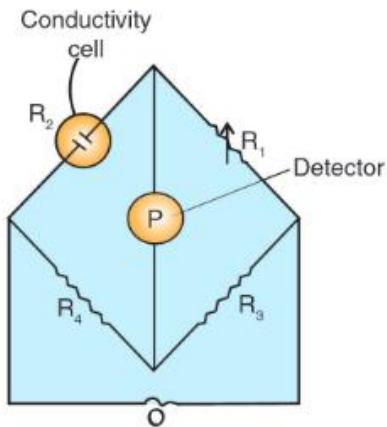


Fig 4.2 Arrangements for measurement of resistance of a solution of an electrolyte

It consists of two resistances R_3 and R_4 , a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 . The Wheatstone bridge fed by an oscillator O (a source of a.c. power in the audio frequency range 550 to 5000 cycles per second). P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions.

$$\text{Unknown resistance } R_2 = \frac{R_1 R_4}{R_3}$$

These days, inexpensive conductivity meters are available which can directly read the conductance or resistance of the solution in the conductivity cell. Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation :

$$K = \frac{\text{cell constant}}{R} = \frac{G^*}{R}$$

In practice, the concentration of solutions of acids or bases or salts is expressed in molarity or in normality. Conductance of electrolytic solution with reference to the concentration is two types: Molar conductance (μ) and equivalent conductance (Λ).

The conductance of a volume of the solution containing one gram mole of electrolyte placed between two parallel electrodes separated by a distance of unit length is called molar conductance.

$$\text{Molar conductivity, } \mu (\text{sm}^2 \text{mol}^{-1}) = \frac{k(\text{sm}^{-1})}{M(\text{mol m}^{-3})} = \frac{k(\text{sm}^{-1})}{1000 \times M(\text{mol L}^{-1})}$$

The conductance of a volume of the solution containing one gram equivalent of the electrolyte placed between two parallel electrodes separated by a distance of unit length is called equivalent conductance.

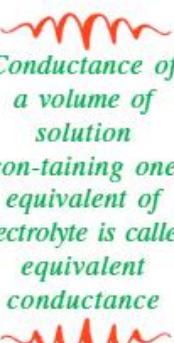
$$\text{Equivalent conductivity, } \Lambda (\text{sm}^2 \text{eq}^{-1}) = \frac{k(\text{sm}^{-1})}{N(\text{eq m}^{-3})} = \frac{k(\text{sm}^{-1})}{1000 \times N(\text{eq L}^{-1})}$$

Units of molar conductance are $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in CGS system and $\text{S m}^2 \text{mol}^{-1}$ in SI system. Units of equivalent conductance are $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$ in CGS system and $\text{S m}^2 \text{eq}^{-1}$ in SI system.

$$1 \text{ sm}^2 \text{mol}^{-1} = 10^4 \text{ scm}^2 \text{mol}^{-1} \text{ (or) } 1 \text{ scm}^2 \text{ mol}^{-1} = 10^{-4} \text{ sm}^2 \text{mol}^{-1}$$

Conductivity, molar conductivity and equivalent conductivity depends on the nature of electrolyte, concentration of electrolyte and temperature. Equivalent conductance or molar conductance decreases with increase in concentration as shown in Fig 4.3.

Greater the number of ions in the solution, greater is the conductance. Strong electrolytes dissociates almost completely into ions but weak electrolytes dissociates to very small extent into ions. Thus, among the same molar concentration solutions of strong electrolytes and weak electrolytes, number of ions is maximum in strong electrolyte solution than that of weak electrolyte. Hence conductivity, molar conductivity and equivalent conductivity are higher for strong electrolyte than weak electrolyte.


*Conductance
a volume of
solution
containing one
equivalent of
electrolyte is called
equivalent
conductance*

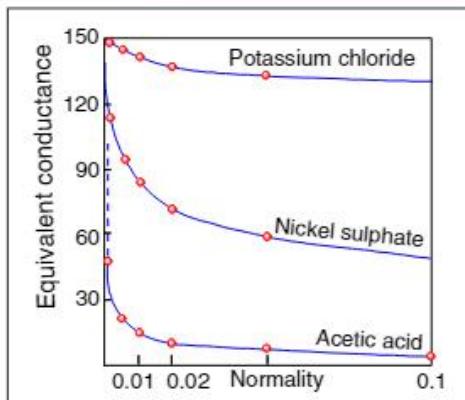


Fig 4.3 Variation of equivalent conductivity with concentration


**Equivalent
conductance
increases upon
dilution**


With an increasing the conductivity, molar conductance and equivalent conductance increases both for strong electrolytes and for weak electrolytes. For weak electrolytes, with increasing the temperature extent of dissociation of weak electrolyte increases and numbers of ion in the solution increases. Thus k , r and u increases.

With dilution (i.e., decreasing the concentration) of electrolyte, molar conductance and equivalent conductance increases but conductivity decreases both for strong electrolytes and weak electrolytes. With dilution of weak electrolyte, extent of dissociation of weak electrolyte increases. Thus total number of ions given by one mole or one equivalent weight of electrolyte increases but number of ions per unit volume of weak electrolyte decreases. Hence, r and u increases but k decreases with dilution for weak electrolytes. Strong electrolytes undergo complete ionisation at all concentrations. Thus for strong electrolytes, with dilution no change in total number of ion but mobility of ions increases oppositely charged ions become far apart from one another. As a result r and u increases with dilution for strong electrolytes. For strong electrolytes also with dilution conductivity decreases due to decreases in number of ions per unit volume.

Specific conductance of electrolytic solution depends upon nature of the electrolyte. Strong electrolytes exhibit high conductance, while weak electrolytes show low conductance at any concentration. Non-electrolytes are called non-conductors as their specific conductances are negligibly small. Specific conductivities of some substances are listed in Table 4.2.

As the concentration decreases for any electrolyte, the equivalent conductance increases. The increase in the conductivity of a weak electrolyte at lower concentrations is attributed to increase in the extent of dissociation. The variation in the equivalent conductance with concentration is not much significant in the case of strong electrolytes. However, more the valency of ion even in a strong electrolyte, more the increase in equivalent conductance with decreasing the concentration of electrolyte.

The ratio of equivalent conductance at any concentration (Λ_c) and at infinite dilution (Λ_0) is called conductance ratio. For a weak electrolyte, the conductance ratio is equal to degree of dissociation.

$$\text{Degree of dissociation, } \alpha = \Lambda_c / \Lambda_0$$


Pure water has
a small
conductivity of
 $3.5 \times 10^{-5} \text{ S m}^{-1}$



Table 4.2 Specific conductivity of some selected materials at 25°C

Material	Conductivity, S m ⁻¹	Material	Conductivity, S m ⁻¹
Conductors		Aqueous solutions	
Sodium	2.1×10^3	0.1 M HCl	3.91
Copper	5.9×10^3	0.01 M KCl	0.14
Silver	6.2×10^3	0.01 M NaCl	0.12
Iron	1.0×10^3	0.1 M HAc	0.047
Graphite	1.2×10	0.01 M HAc	0.016
Semiconductors		Pure water	3.5×10^{-5}
CuO	10×10^{-7}	Insulators	
Si	1.5×10^{-2}	Glass	1.0×10^{-16}
Ge	2.0	Teflon	1.0×10^{-18}

4.1.4

Kohlrausch law


A plot of
 Λ vs \sqrt{c} on
extrapolation
gives equivalent
conductance at
infinite dilution



Equivalent conductance of an electrolytic solution at very low concentration is known as equivalent conductance at infinite dilution or at zero concentration or limiting equivalent conductance (Λ_0). Direct determination of conductance at zero concentration of solution is not practically possible. The work of Debye and Huckel on the quantitative treatment of the equivalent conductance, marked the commencement of a new era in electrochemistry.

For strong electrolytes Λ vs \sqrt{c} graph is a straight line with negative slope as shown in Fig 4.4. For strong electrolytes, limiting equivalent conductance can be known by extrapolating Λ vs \sqrt{c} graph to zero concentration. For weak electrolytes, limiting equivalent conductance cannot be calculated from Λ vs \sqrt{c} graph. Because for weak electrolytes, at low concentrations, Λ increases sharply with decreasing the concentration. For weak electrolytes, Λ_0 is indirectly calculated from Kohlrausch law.

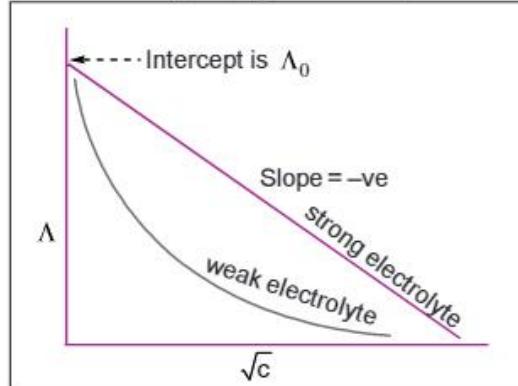


Fig 4.4 Variation of equivalent conductance with square root of concentration

When the equivalent conductance at infinite dilution of pairs of salts having an ion in common are examined, certain regularities are evident. From the results of Table 4.3, the difference in equivalent conductance of sodium and potassium salts of the same anion is independent of the nature of the latter. The phenomenon discovered


Independent migration of ions is the basis for Kohlrausch law



Equivalent conductance at infinite dilution is the sum of the equivalent conductances of ions



Conductivity of proton is highest at infinite dialution, due to small size of ion


by Kohlrausch was ascribed to the fact that each ion contributes a definite amount to the total conductance of the electrolyte, irrespective of the nature of other ion. This is known as law of independent migration of ions and is true only at infinite dilution when there are no mutual ionic interactions.

Table 4.3 Equivalent conductance ($\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$) at infinite dilution at 18°C

Electrolyte	Equivalent conductance	Electrolyte	Equivalent Conductance	Difference
KCl	130.0	NaCl	108.9	21.1
KNO ₃	126.3	NaNO ₃	105.2	21.1
K ₂ SO ₄	133.0	Na ₂ SO ₄	111.9	21.1

Kohlrausch law states that the equivalent conductance at infinite dilution of an electrolyte is equal to the algebraic sum of equivalent conductivities of the ions at infinite dilution of electrolyte.

If λ_+^0 and λ_-^0 are ionic conductivities, at infinite dilution for cation and anion, Kohlrausch law may be expressed in the form, $\Lambda_0 = \lambda_+^0 + \lambda_-^0$.

$$\mu_0 = n_+ \cdot \mu_+^0 + n_- \cdot \mu_-^0$$

$$\Lambda_0 \text{Al}_2(\text{SO}_4)_3 = \Lambda_0 \text{Al}^{3+} + \Lambda_0 \text{SO}_4^{2-}$$

$$\mu_0 \text{Al}_2(\text{SO}_4)_3 = 2\mu_0 \text{Al}^{3+} + 3\mu_0 \text{SO}_4^{2-}$$

Ionic conductances at infinite dilution for some cations and anions are listed in Table 4.4. Proton (H^+) is an ion with abnormally smaller size, has highest mobility and has highest conductance at infinite dilution. Equivalent conductance of ions decreases with increase in the size of hydrated ions and also with an increase in the valency of the ion.

Table 4.4 Conductances of ions at infinite dilution at 25°C

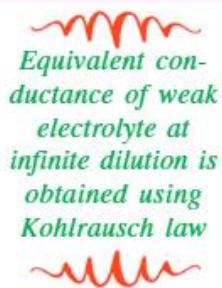
Cation	$\lambda_+, \text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$	Anion	$\lambda_-, \text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$
H^+	349.8	OH^-	198.5
Li^+	38.7	Cl^-	76.3
Na^+	50.4	Br^-	78.4
K^+	71.5	I^-	76.8
Ag^+	61.9	NO_3^-	71.4
NH_4^+	73.4	CH_3COO^-	40.9
Mg^{2+}	53.1	SO_4^{2-}	79.8

Ionic conductance at infinite dilution (Λ_+^0 and Λ_-^0) are directly proportional to their ionic mobilities (μ_+^0 and μ_-^0)

$$\Lambda_+^0 \propto \mu_+^0 \text{ and } \Lambda_-^0 \propto \mu_-^0 ; \Lambda_+^0 = F\mu_+^0 \text{ and } \Lambda_-^0 = F\mu_-^0$$

$$\Lambda^0_{\text{electrolyte}} = F(\mu_+^0 + \mu_-^0), \text{ where } F = 96,500 \text{ C}$$

HCl, NaCl and CH_3COONa are all strong electrolytes and their equivalent conductivities are measured.


Equivalent conductance of weak electrolyte at infinite dilution is obtained using Kohlrausch law

Kohlrausch law of independent mobilities of ions is applied to calculate the equivalent conductivity of weak electrolyte like acetic acid.

$$\Lambda_0^{\text{CH}_3\text{COONa}} + \Lambda_0^{\text{HCl}} - \Lambda_0^{\text{NaCl}} =$$

$$\Lambda_0^{\text{CH}_3\text{COO}^-} + \Lambda_0^{\text{Na}^+} + \Lambda_0^{\text{H}^+} + \Lambda_0^{\text{Cl}^-} - \Lambda_0^{\text{Na}^+} - \Lambda_0^{\text{Cl}^-} =$$

Therefore,

$$\Lambda_0^{\text{CH}_3\text{COO}^-} + \Lambda_0^{\text{H}^+} = \Lambda_0^{\text{CH}_3\text{COOH}}$$



- P.4.1** BaSO₄ is ionic and PCl₃ is covalent but a saturated solution of BaSO₄ is a weak electrolyte, while that of PCl₃ is a strong electrolyte. Explain.

Solution BaSO₄ has high lattice energy. It is very less soluble in water, even in saturated solutions. The ionic concentration is in the order of 10⁻⁵ M. Hence it is a weak electrolyte.

PCl₃ is covalent. It undergoes hydrolysis in water to give hydrochloric acid, which is a strong electrolyte.



- P.4.2** A column of 0.05 M NaOH solution of diameter 1cm and length 1m has resistance 1.11×10^4 ohm. Calculate the resistivity, conductivity and molar conductivity.

Solution Area = $a = \pi r^2 = (22/7)(0.5 \text{ cm})^2 = 7.85 \times 10^{-5} \text{ m}^2$.

Length = $l = 1 \text{ m}$.

Resistance = $R = 1.11 \times 10^4$.

$$\text{Resistivity} = \rho = R \frac{a}{l} = \frac{1.11 \times 10^4 \times 7.85 \times 10^{-5}}{1} = 0.871 \Omega \text{m}$$

$$\text{Conductivity} = k = \rho^{-1} = (0.871 \text{ ohm m})^{-1} = 1.15 \text{ S m}^{-1}$$

$$\text{Molar conductivity} = \mu = \frac{k \times 1000}{\text{molarity}} = \frac{1.15 \times 1000}{0.05} = 2.3 \times 10^4 \text{ S m}^2 \text{ mol}^{-1}$$



- P.4.3** The conductivity of 0.1 M KCl solution is 1.29 S m⁻¹. If the resistance of the cell filled with 0.1 M KCl is 100 Ω, calculate the cell constant.

Solution The cell constant filled with electrolytic solution is given as,

Cell constant = specific conductivity × resistance.

$$\begin{aligned} \text{Cell constant} &= 1.29 \text{ S m}^{-1} \times 100 \Omega \\ &= 1.29 \text{ m}^{-1} = 129 \text{ cm}^{-1} \end{aligned}$$



- P.4.4** It is practically difficult to calculate the equivalent conductivity of a weak electrolyte in aqueous solutions. Comment.

Solution Equivalent conductance = (k × 1000) / normality.

The extent of dissociation of a weak electrolyte is less. Accordingly the number of ions furnished in aqueous solutions is less.

The specific conductivity (k) of a weak electrolyte is in the order of 10⁻² S m⁻¹ or less. Since k is less, it is difficult to calculate equivalent conductivity of a weak electrolyte.



- P.4.5** Using Kohlrausch law, calculate Λ_0 for acetic acid, if Λ_0 values for hydrochloric acid, sodium chloride and sodium acetate are respectively 426, 126 and 91 S cm² mol⁻¹.

Solution Λ_0 of acetic acid = Λ_0 of CH₃COO⁻ + Λ_0 of H⁺ =

$$\begin{aligned} \Lambda_0 \text{ of HCl} + \Lambda_0 \text{ of CH}_3\text{COONa} - \Lambda_0 \text{ of NaCl} \\ = 426 + 91 - 126 \\ = 391 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$



P.4.6 Equivalent conductivity of a weak acid HA at infinite dilution is $390 \text{ S cm}^2 \text{ eq}^{-1}$. Conductivity of $1 \times 10^{-3} \text{ N}$ HA solution is $4.9 \times 10^{-5} \text{ S cm}^{-1}$. Calculate the extent of dissociation and dissociation constant of the acid.

Solution Equivalent conductivity of $1 \times 10^{-3} \text{ N}$ HA solution (Λ_m) = $k / \text{normality}$.

$$\Lambda_c = \frac{4.9 \times 10^{-5} \times 1000}{1 \times 10^{-3}} = 49 \text{ S cm}^2 \text{ eq}^{-1}$$

Equivalent conductance at infinite dilution (Λ_0) = $390 \text{ S cm}^2 \text{ eq}^{-1}$.

$$\text{Extent of dissociation} = \alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{49}{390} = 0.126$$

$$\text{Dissociation constant of acid} = K_a^2 = 1 \times 10^{-3} (0.126)^2 = 1.5 \times 10^{-5} \text{ mol L}^{-1}$$

EXERCISE - 4.1.1

1. Write the types of electrical conductors with suitable examples.
2. What is degree of dissociation? How is it useful to distinguish between strong and weak electrolytes?
3. Define the terms resistance, resistivity, conductance and specific conductance. Write their units.
4. Discuss (a) molar conductance and (b) equivalent conductance.
5. Why does the conductivity of a solution decrease with dilution?
6. Suggest a way to determine the Λ_m^0 value of water.
7. How is the conductance of an electrolytic solution influenced by various factors?
8. State and explain the Kohlrausch law of independent migration of ions.
9. At 25°C , the specific conductance of 0.01 M alkaline earth metal chloride is $0.000158 \text{ ohm}^{-1} \text{ cm}^{-1}$. Calculate the equivalent conductance.
(Ans : $7.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$)
10. Calculate the limiting molar conductivities of
a) magnesium sulphate and b) calcium chloride.
Limiting molar conductivity of Mg^{2+} , Ca^{2+} , SO_4^{2-} and Cl^- are respectively 106, 119, 160 and $76.3 \text{ scn mol}^{-1}$ (Ans : $266 \text{ scn}^2 \text{ mol}^{-1}$; $27.16 \text{ S cm}^2 \text{ mol}^{-1}$)
11. Calculate the equivalent conductance of NH_4OH at infinite dilution using Kohlrausch law. Given that Λ_0 values of NaOH , NaCl and NH_4Cl are respectively 217.4, 108.9 and $129.8 \text{ ohm}^{-1} \text{ cm}^2$. (Ans : $238 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$)
12. The conductivity of $0.001028 \text{ mol L}^{-1}$ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.
(Ans : $1.75 \times 10^{-5} \text{ mol L}^{-1}$)
13. The molar conductivity of 0.025 mol L^{-1} methanoic acid is $46.1 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^0(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$
(Ans : 0.114 ; $3.67 \times 10^{-4} \text{ mol L}^{-1}$)
14. At 25°C equivalent conductance of a weak acid HAc is $16.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$. If the ionic conductances of Ac^- and H^+ at infinite dilution are respectively 40.9 and $349.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$, calculate the percentage dissociation of the weak acid at 25°C .
(Ans : 4.1%)

ELECTROLYSIS

Sodium combines with chlorine directly to form sodium chloride. The reaction involves oxidation of Na to Na^+ and reduction of Cl to Cl^- . Thus the reaction between a metal and a non-metal is described as a redox reaction.

The formation of sodium chloride from its elements is an example of spontaneous change. The process of getting back the elements from an electrolyte involves a non-spontaneous redox reaction. Such a process is made possible using electrical energy.

4.2.1

Electrolysis phenomenon


Electrolysis is the process of decomposition of a substance by applied EMF


The decomposition of a chemical compound in the molten state or solution state into its constituent elements under the influence of an applied electromotive force (EMF) is called electrolysis. Electrolysis is a typical example of redox reaction. It means the decomposition of a chemical substance by applied EMF.

Electrolysis is performed in a device called electrolytic cell. Electrons enter into the cell at cathode and hence it is negatively charged. Electrons flow in the external circuit from anode to cathode.

Positively charged ions migrate towards the negative electrode and negatively charged ions migrate towards the positive electrode. The ionic velocities are actually only slightly greater than random molecular speeds. A common setup of electrolysis is shown in Fig 4.5.

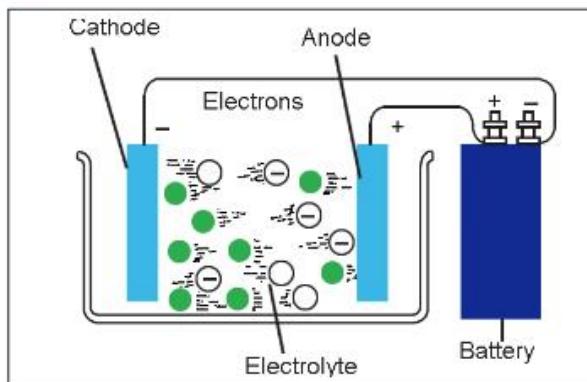


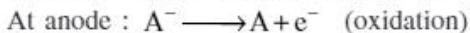
Fig 4.5 Experimental setup of electrolysis

During electrolysis, the cations move towards the negative electrode, cathode and the anions move towards the positive electrode, anode. They get discharged and get deposited.

Let BA be an electrolyte, containing B^+ and A^- ions. During electrolysis, B^+ ions move towards cathode whereas A^- ions move towards anode.



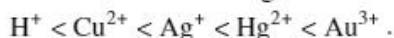
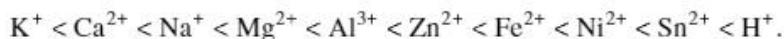
At cathode, gain of electrons, electronation or reduction takes place.



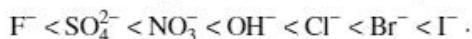
At anode, loss of electrons, deelectronation or oxidation takes place.

During electrolysis the electrons enter into the electrolyte at cathode and they are taken up by the cations. The electrons lost by the anions leave the electrolyte at anode. As a result, ions are converted into atoms or molecules and get deposited or liberated at respective electrodes.

The increasing order of ease of deposition of some cations :

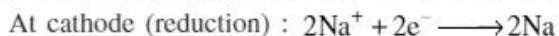


The increasing order of ease of deposition of some anions :

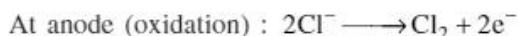


The process is illustrated by taking the electrolysis of molten sodium chloride as an example.

When electric current is passed through molten sodium chloride, the Na^+ ions move towards the cathode and the Cl^- ions move towards the anode.



Sodium ions are reduced and sodium metal (Na) is deposited at cathode.



Chloride ions are oxidised and Cl_2 gas is liberated at anode.

4.2.2

Examples and applications

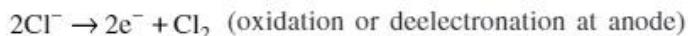

At cathode electrolysis of fused NaCl gives Na and aqueous NaOH gives H_2


Electrolysis of fused and aqueous solutions at inert electrodes is made use of producing generally metal at cathode and non-metal at anode. Though hydrogen is a non-metal, it is electrolytically extracted at cathode from aqueous solutions. However, hydrogen is liberated at anode during the electrolysis of fused metal hydrides.

The electrolysis of aqueous sodium chloride solution differs from that of molten sodium chloride. Ionisation of aqueous salt solution produces Na^+ and Cl^- ions. Na^+ ions travel to the cathode but cannot undergo reduction to metal at platinum cathode in aqueous solutions. Water preferentially undergoes reduction to give hydrogen gas.

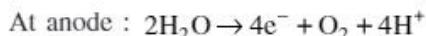
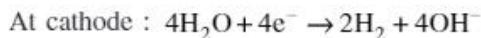


Chloride ions travel to the anode and undergo oxidation to give chlorine gas.

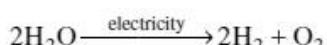


However, on prolonged electrolysis, when most of the chloride ions are oxidised, water is oxidised finally to liberate oxygen gas at anode.

Electrolysis of water, using platinum electrodes liberates hydrogen at cathode and oxygen at anode. Water is a very poor electrolyte. In order to increase the conductivity a small amount of an electrolyte is dissolved in water during electrolysis.



The overall reaction is :



The products of electrolysis at inert electrodes are the same using dilute sulphuric acid solution, using dilute caustic soda solution or using an aqueous potassium sulphate solution as electrolyte.

Some more examples of electrolysis reactions and the products obtained at the respective electrodes are summarised in Table 4.5.

Table 4.5 Some examples of electrolysis of substances and the respective products

Electrolyte used	Anode used	Anode reaction	Anode used	Cathode reaction
Fused NaCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. NaCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Hg	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. NaCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Fused NaOH	Pt	$4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$	Pt	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. NaOH	Pt	$4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Aq. HCl	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Aq. H_2SO_4	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
50% H_2SO_4	Pt	$2\text{HSO}_4^- \rightarrow \text{H}_2\text{S}_2\text{O}_8 + 2\text{e}^-$	Pb	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Aq. Na_2SO_4	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
Fused CuCl_2	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Aq. CuCl_2	Pt	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Aq. CuCl_2	Cu	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Aq. CuSO_4	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Fused MgCl_2	C	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	Steel	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$
Fused MgO	C	$2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$	Fe	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$
Fused NaH	Pt	$2\text{H}^- \rightarrow \text{H}_2 + 2\text{e}^-$	Pt	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
Aq. AgNO_3	Pt	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	Pt	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$
Aq. AgNO_3	Ag	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$
Aq. ZnSO_4	Zn	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$

Applications of electrolysis :

- a) Electrorefining of metals : Metals like Cu, Ag, Au, Al, Sn, etc., can be purified by electrolysis.
- b) Electroplating: Electroplating is the deposition of precious metals (Au, Ag, Pt, etc.) on less expensive metals (like Cu and Fe). The process of electroplating is carried out by electrolysis.
- c) Electrometallurgy: Active metals like Na, K, Mg, Al, etc., are obtained by the electrolysis of corresponding fused electrolytes.
- d) Manufacture of non metals: Electrolysis has been employed in the manufacture of non-metals, like hydrogen, oxygen, chlorine, fluorine, etc.
- e) Manufacture of compounds: Large scale production of NaOH, KOH, KCl, Na_2CO_3 , D_2O , H_2O_2 , etc., can be carried out by electrolysis.
- f) Tinning: Tinning is the coating of tin over iron or steel sheets which are used for manufacturing containers for storing food stuff.


**Electrometallurgy
is used to extract
active metals like
Na, K, Mg and Al**


4.2.3**Faraday's laws**


Amount of substance liberated at an electrode is proportional to the quantity of electricity


Faraday put forward two laws regarding the quantity of electricity passed through electrolytes and the amounts of substance deposited or liberated at electrodes.

These laws are also known as fundamental laws of electrochemistry and are called quantitative relationships of electrolysis. These laws are applicable to all electrolytes at all the temperatures, pressures and other conditions.

First law : The amount of substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.

The first law is mathematically expressed as,

$$w \propto Q$$

where, w = weight of the substance in grams

Q = quantity of electricity in coulombs

$$Q = i \times t$$

i = current strength in amperes

t = time in seconds

$$w \propto i \times t \text{ (or) } w = e \times i \times t \text{ (or) } e = w/(i \times t)$$

where 'e' is a constant known as electrochemical equivalent and is the characteristic of the substance deposited.

If $Q = 1$ coulomb, then $e = w$

Electrochemical equivalent may be defined as the amount of substance deposited by passing one coulomb of electricity through the electrolyte. It is also defined as the amount of substance deposited by passing a current strength of one ampere for one second. The units of electrochemical equivalent are : gram / ampere-second or gram / coulomb. The SI units of electrochemical equivalent are kg coul⁻¹.

Second law : If the same quantity of electricity is passed through different electrolytes, then the weight of substances deposited at the respective electrodes are in the ratio of their chemical equivalents.

The second law is mathematically expressed as,

$$w \propto E$$

where 'E' is the equivalent weight of the substance.

If the same quantity of electricity is passed through two or more different electrolytes, the second law is applied. Let the weight of the substance 'A' be w_A and equivalent weight of 'A' be E_A . Let the weight of the substance, 'B' be w_B and equivalent weight of 'B' be E_B .

Then, according to the second law,

$$\frac{w_A}{w_B} = \frac{E_A}{E_B} \text{ or } \frac{w_A}{E_A} = \frac{w_B}{E_B}$$

Let us consider that three cells containing dilute sulphuric acid, aqueous copper sulphate and silver nitrate solutions are connected in series as shown in Fig 4.6. If the same quantity of electricity is passed through these cells, the amounts of hydrogen gas, silver metal and copper metal deposited at the respective electrodes are in the ratio of their equivalent weights.


Masses of substances liberated at electrodes in series are in the ratio of their equivalent masses

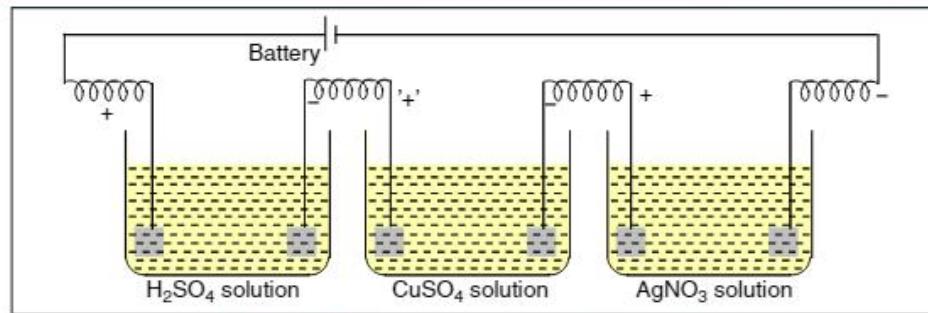



Fig 4.6 Voltameters arranged in series

Based on the second law of Faraday,

$$\frac{\text{weight of H}}{\text{equivalent weight of H}} = \frac{\text{weight of Ag}}{\text{equivalent weight of Ag}} = \frac{\text{weight of Cu}}{\text{equivalent weight of Cu}}$$

Substituting equivalent weights of hydrogen, silver and copper,

$$\frac{\text{weight of hydrogen}}{1.008} = \frac{\text{weight of Ag}}{108} = \frac{\text{weight of Cu}}{31.75}$$

Combining the two Faraday's laws

$w \propto E \times i \times t$, first law and $w \propto E$, second law

$w \propto E \times i \times t$ (or)

$$w = \frac{1}{F} \times E \times i \times t$$

where F is the proportionality constant called Faraday.

If $w = E$, $F = it$. Faraday is defined as the quantity of electricity required to deposit or to dissolve one gram equivalent weight of a substance.

The total charge present on one mole of electrons is known as Faraday.

Both coulomb and Faraday are the units of quantity of electricity. Coulomb represents a smaller quantity and Faraday represents a larger quantity of electricity.

$$\begin{aligned} \text{One Faraday} &= \text{Charge of one mole of electrons} = \text{Charge of } 6.023 \times 10^{23} \text{ electrons} \\ &= 6.023 \times 1.602 \times 10^{-19} \text{ coulomb} = 96488 \text{ coulomb.} \end{aligned}$$

One Faraday is usually taken as 96500 coulomb.

Electrochemical equivalent (e) is

$$e = \frac{\text{Equivalent weight}}{96,500} \quad (\text{or}) \quad e = \frac{\text{Atomic weight}}{n \times 96,500}$$

Here n is the valency of the substance and is called number of Faradays.

Faraday's laws of electrolysis are useful for the determination of the amounts of substances deposited, the quantity of electricity, the number of electrons passing through the electrolyte, equivalent weights, atomic weights and valency.

The charge of one gram ion of cuprous copper is 1 Faraday.

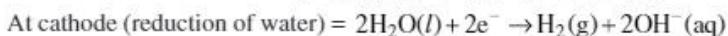
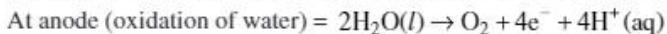
The charge of one gram ion of ferric iron is 3 Faradays.

To deposit one gram atom of a metal with valence 'n' or to undergo chemical reaction of one mole of a compound with valence 'n', n Farady's of electricity is required.



P.4.7 Electrolysis of aqueous potassium sulphate containing litmus, develops red colour at anode and blue colour at cathode. Why?

Solution During the electrolysis of aqueous K_2SO_4 , the chemical changes involved are,

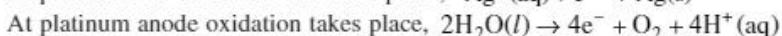


Solution is acidic around anode and litmus is red. Solution is basic around cathode and litmus is blue.



P.4.8 Aqueous silver nitrate is subjected to electrolysis, using platinum electrodes. What will be the nature of the solution after some time?

Solution At platinum cathode reduction takes place, $Ag^+(aq) + e^- \rightarrow Ag(s)$



As a result of the conversion of water to proton, the solution becomes acidic (nitric acid). The pH of the solution decreases.



P.4.9 Calculate the equivalent weight and electrochemical equivalent of copper deposited from cupric salt (At.wt. of Cu = 63.5).

Solution Deposition of Cu from cupric salt electrolytically is given as, $Cu^{2+} + 2e^- \rightarrow Cu$

$$\text{Equivalent weight of copper} = \frac{\text{Atomic weight}}{\text{Number of Faraday}} = \frac{63.5}{2} = 31.75$$

$$\text{Electrochemical equivalent of copper} = \frac{\text{Equivalent weight}}{96,500} = \frac{31.75}{96,500} = 3.29 \times 10^{-4} \text{ g coul}^{-1}$$



P.4.10 If a current of one ampere flows through a metal wire for one hour, how many electrons would flow through the wire?

Solution Current strength (i) = 1 amp ; time (t) = 1hr = 3600 s

Quantity of electricity (Q) = $1 \times 3600 = 3600$ coul.

96500 Coul = Avogadro number of electrons

$$\text{Number of electrons flown through the wire} = \frac{\text{Avogadro number}}{\text{Quantity of electricity}} = 6.023 \times 10^{23} \times \frac{3600}{96500} = 2.246 \times 10^{21} \text{ electrons.}$$



P.4.11 Find the total charge in coulomb on one gram ion of nitride.

Solution Charge on each nitride (N^{3-}) ion = $3 \times 1.602 \times 10^{-19} = 4.806 \times 10^{-19}$ coul.

Number of ions in a gram ion of nitride = 6.023×10^{23}

Total charge on one gram ion of nitride = $6.023 \times 10^{23} \times 4.806 \times 10^{-19} = 2.895 \times 10^5$ coul.



P.4.12 What is the ratio of (a) gram atoms and (b) weights of the metals liberated during the electrolysis of fused sodium fluoride, magnesium fluoride and aluminium fluoride connected in a series?

Solution $Na^+ + e^- \rightarrow Na$; $Mg^{2+} + 2e^- \rightarrow Mg$ and $Al^{3+} + 3e^- \rightarrow Al$

$$\text{Ratio of gram atoms of metals liberated using one Faraday} = \frac{1}{1} : \frac{1}{2} : \frac{1}{3} = 6 : 3 : 2$$

$$\text{Ratio of weights of metals liberated} = 6 \times 23 : 3 \times 24 : 2 \times 27 = 23 : 12 : 9$$



P.4.13 A solution of copper sulphate is electrolysed using a current strength of 3 amp to deposit 60 grams of copper. What is the time taken for the electrolysis?

Solution Deposition of copper is given as : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

2 Faradays or 193000 coulomb can deposit 63.5 grams of copper.

$$\text{Quantity of electricity (Q) required to deposit 60 grams of copper} = \frac{60}{63.5} \times 193000 = 182362 \text{ coul.}$$

$$\text{Time taken for the electrolysis (t)} = \frac{Q}{i} = \frac{182362}{3} = 60787 \text{ sec} = 16.9 \text{ hrs.}$$



P.4.14 An oxide of metal (at.wt. = 112) contains 12.5% of oxygen by weight. What is the valency of metal? What mass of the metal will be liberated when the oxide is converted to chloride with HCl and electrolysed using a current of 9.65 amp for a period of 30 min?

Solution Equivalent of oxygen = Equivalent of metal

$$\frac{12.5}{8} = \frac{87.5}{E}, \text{ where } E \text{ is the equivalent weight of metal, } E = 56.$$

$$\text{Valency of metal} = \text{At. wt./Eq. wt.} = 112/56 = 2.$$

$$\text{Mass of the metal deposited} = \frac{E \times i \times t}{96500} = \frac{56 \times 9.65 \times 30 \times 60}{96500} = 10.08 \text{ g.}$$



P.4.15 The electrical expenditure is two rupees to produce one gram of calcium from fused CaSO_4 . What is the production cost of 2 grams of hydrogen produced electrically from acidulated water?

Solution $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca(s)}$ and $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

2 Faradays are required to deposit 40g of Ca or to liberate 2g of hydrogen.

$$\text{Cost incurred in producing 2g of hydrogen} = \frac{40\text{g}}{1\text{g}} \times 2 = 80 \text{ rupees.}$$



P.4.16 Calculate the quantity of electricity needed to reduce one centimole of dichromate in acid medium, to chromic state.

Solution The stoichiometric equation is, $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

One mole of dichromate = 6 moles of electrons = 579000 coul.

Quantity of electricity required to reduce one centimole of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} = 5790 coul.



P.4.17 A 200W, 110V incandescent lamp was connected with an electrolytic cell containing ZnCl_2 . What weight of metal will be deposited on passing current for 1 hour? (At. wt. of Zn = 65.4).

Solution Current strength in ampere = Watt/Volt = $200/110 = 1.818$

Time = $1 \times 60 \times 60 = 3600$ sec ; Quantity of electricity = $1.818 \times 3600 = 6545$ coul.

Zinc is divalent. 193000 coul are required to deposit 65.4g of zinc.

$$\text{Weight of metal deposited using 6545 coul} = \frac{6545 \times 65.4}{193000} = 2.219 \text{ g.}$$



P.4.18 During the electrolysis of fused potassium chloride at platinum electrodes, 0.25 gram atom of metal is liberated. What would be the volume of chlorine that can be collected in the experiment at STP?

Solution Reaction at cathode, $\text{K}^+ + \text{e}^- \rightarrow \text{K}$ and at anode, $2\text{Cl}^- \rightarrow 2\text{e}^- + \text{Cl}_2$

For every one gram atom of potassium liberated, 0.5 mol of chlorine is released.

For 0.25 gram atom of potassium liberated, moles of chlorine released = 0.125.

Volume of chlorine released in the experiment at STP = $0.125 \times 22.4 = 2.8 \text{ L.}$



P.4.19 Density of silver metal is 10.8 g cc^{-1} . A $20 \times 10 \text{ cm}$ thin iron foil is totally immersed in aqueous silver nitrate. Making it as cathode, electrolysis is done using a current strength of 1930 amp for a period of 100 sec. Calculate the thickness of silver metal electroplated on each face of iron foil.

Solution Quantity of electricity (Q) = $i t = 1930 \times 100 = 193000$ coul.

$$\text{Amount of silver deposited using 193000 coul} = \frac{193000 \times 108}{96500} = 216 \text{ g}$$

Amount of silver deposited on each face of the iron foil = 108 g

$$\text{Volume of silver electroplated on each face of the iron foil} = \frac{w}{d} = \frac{108}{10.8} = 10 \text{ cc}$$

The volume is given as, $v = (l + b) \times t$, if (t) is the thickness and (l × b) is area.

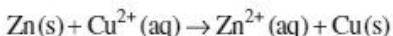
$$\text{Thickness of silver electroplated} = \frac{\text{volume}}{\text{area}} = \frac{10}{20 \times 10} = 0.05 \text{ cm} = 0.5 \text{ mm.}$$

EXERCISE - 4.1.2

1. Describe the phenomenon electrolysis with the help of two examples.
2. Write the important applications and uses of electrolysis.
3. State and explain Faraday's laws of electrolysis.
4. Find the ratio of electrochemical equivalents of silver and aluminium.
(Ans : 12:1)
5. How many hours are needed to deposit the metal based on the reaction,
 $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$, using a current strength of 0.02 amp. (Ans : 268 hr)
6. Calculate the electrochemical equivalent of the lightest element.
(Ans : $1.045 \times 10^{-5} \text{ g coul}^{-1}$)
7. Suggest a list of metals that are extracted electrolytically.
8. A metal wire carries a current of one amp. How many electrons pass a point in the wire in one sec.
(Ans : 6.24×10^{18})
9. A solution of CuSO_4 is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? (Ans : 0.294 g)
10. 16 grams of copper sulphate is dissolved in one litre of water. It is electrolysed using a current strength of 10 amp for a period of 965 sec. What is the concentration of copper sulphate after electrolysis? Take atomic weight of copper as 64 and assume there is no loss in water during electrolysis. (Ans : 0.05M)
11. 3g of metal ions were discharged at cathode using a current of 3 amperes for 2 hours from aqueous cupric sulphate solution. Calculate the current efficiency. At wt. of Cu is 63.5.
(Ans : 42.2 %)
12. Calculate the current in amperes required to liberate 10g of silver electrolytically in one hour from AgNO_3 solution.
(Ans : 2.28 amp)
13. Same quantity of electrical charge that deposited 0.583g of silver was passed through a solution of gold salt. If 0.335g of gold is deposited, calculate the oxidation state of gold in the given salt. At. wt. of Au = 197. (Ans : +3)

GALVANIC CELLS**4.3.1****Voltaic cell**

When plates of two dissimilar metals are placed in a conducting liquid such as an aqueous solution of a salt, the resulting system becomes a source of electricity. When a piece of zinc is kept in copper sulphate solution for some time, the zinc piece is turned red. This is due to the deposition of copper on zinc. The reaction is given as,



In this redox reaction two electrons are transferred from zinc atom to cupric ion. The transfer of electrons does not appear as the reactants are mixed together. Electrons can be obtained in such a reaction by modifying the reaction conditions. A device in which electrical energy is generated by performing a chemical reaction is called galvanic cell. Such a cell is also called voltaic cell.

A device in which an electrochemical reaction operates is called an electrochemical cell. It is of two types : (1) electrolytic cell and (2) galvanic cell. Electrical energy is converted into chemical energy in an electrolytic cell. Chemical energy is converted into electrical energy in a galvanic cell. A galvanic cell can be reversed to function

Galvanic cell is a device in which chemical energy is converted into electrical energy



as an electrolytic cell. Galvanic cell is commonly called electrochemical cell. A typical galvanic cell is shown in Fig 4.7.

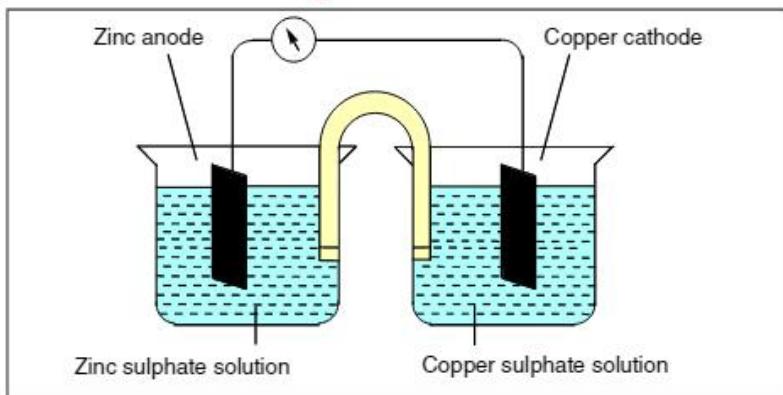


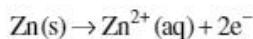
Fig 4.7 Galvanic cell

A galvanic cell consists of two half cells or electrodes. One electrode contains Zn metal plate dipped in ZnSO_4 solution and the other is copper plate in CuSO_4 solution. The two half cells are joined by a salt bridge.

When the Zn and Cu electrodes are joined externally by a wire the following observations are made:

1. There is a flow of electric current through the external circuit.
2. 'Zn' rod loses its mass, while 'Cu' rod gains the mass.
3. The concentration of ZnSO_4 solution increases, while the concentration of CuSO_4 solution decreases.
4. The solutions in both the compartments remain electrically neutral.

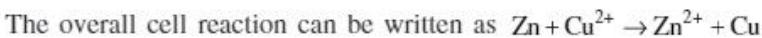
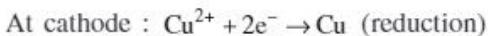
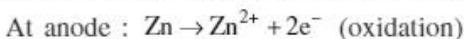
Chemical reactions in a galvanic cell : Zinc goes into solution as Zn^{2+} ions in the half cell in the left hand side.



Since the reaction involves the loss of electrons, it is known as oxidation half reaction. This electrode is known as anode. The electrons from the Zn electrode flow through the external wire to the Cu electrode. Cu^{2+} ions of the CuSO_4 solution take up these electrons to form Cu atoms.



Since this reaction involves gain of electrons it is known as reduction half reaction. This electrode is known as cathode.



Voltmeter is used to measure the potential difference between the two electrodes.

Salt bridge : Salt bridge is an inverted 'U' shaped tube filled with a jelly like substance agar-agar, mixed with an electrolyte like KCl , KNO_3 or some times NH_4NO_3 . These electrolytes are not involved in any electrochemical change and do not react chemically with the electrolytes in the two half cells. The salt bridge minimises the polarisation of the cell and maintains the electrical neutrality of the cell.

Zn atom loses electrons and is called oxidation half-reaction
Cu²⁺ ion gains electrons and is called reduction half-reaction

Daniell cell is designed to make use of spontaneous redox reaction between zinc metal and aqueous cupric ions. A commercial form of Daniell cell is shown in Fig 4.8.

*Spontaneous
redox reaction in
Daniell cell is,
 $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$*

In the Deniell cell the salt bridge is replaced with a porous pot. Aqueous zinc sulphate is taken in the outer vessel. A zinc plate kept in this solution acts as anode. Aqueous copper sulphate is taken in the inner porous vessel. A copper rod kept in this solution acts as cathode. The electrical neutrality of the Daniell cell is maintained by the porous vessel. The net cell reactions is, $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

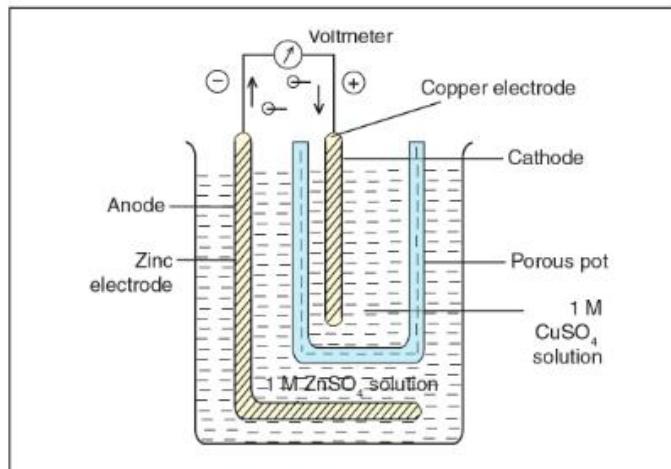


Fig 4.8 Daniell cell

*Standard EMF
of Daniel cell is
1.1 V*

The standard EMF of the Daniell cell is 1.1 V. If an external potential of 1.1 V is applied on this cell, there will be no chemical reaction and no flow of electrons. If the external potential is less than 1.1 V, the spontaneous redox reaction continues. If the external potential is more than 1.1 V, the cell functions as an electrolytic cell and the electrical energy is used to carry non-spontaneous chemical reactions. Functioning of Daniell cell with applied external voltage is shown in Fig 4.9 (a) and in Fig 4.9 (b)

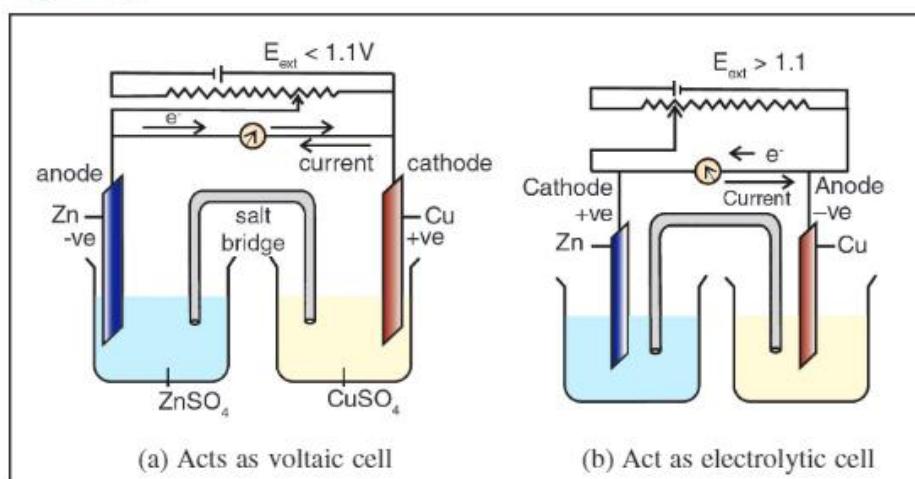


Fig 4.9 Daniell cell with applied external voltage less than 1.1 V (a) and voltage more than 1.1 V (b)

4.3.2**Electrodes and cell notation**

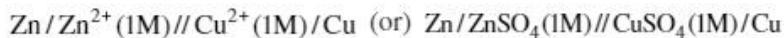
Each electrochemical cell consists of two half cells called as electrodes. Electricity is used to perform a chemical reaction in an electrolytic cell and electricity is generated by performing a chemical reaction in a galvanic cell. The comparison between the two types of cells is given in Table 4.6.

Table 4.6 Comparison between the two types of electrochemical cells

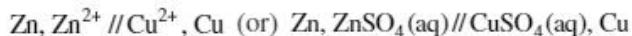
Electrolytic cell	Galvanic cell
1. Electrical energy is converted to chemical energy.	1. Chemical energy is converted to electrical energy.
2. Anode is positively charged.	2. Cathode is positively charged.
3. Cathode is negatively charged.	3. Anode is negatively charged.
4. Oxidation occurs at anode.	4. Oxidation occurs at anode.
5. Reduction occurs at cathode.	5. Reduction occurs at cathode.
6. Electricity flows from the circuit to the cell.	6. Electricity flows from the cell to the circuit.
7. Irreversible and not spontaneous	7. Usually reversible and spontaneous
8. Ions are discharged on both the electrodes.	8. Ions are discharged only on cathode.

Galvanic cell is represented by writing anode on the left hand side and cathode on the right hand side. These two half cells are separated by double vertical line which represents salt bridge.

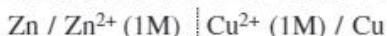
Oxidation half cell // reduction half cell.



The galvanic cell sometimes is also represented as :



If salt bridge is replaced by a porous diaphragm in the Daniell cell, the double vertical line is replaced by single vertical broken line.



Daniell cell is also represented as $\text{Zn}, \text{Zn}^{2+} \mid \text{Cu}^{2+}, \text{Cu}$.

4.3.3**Single electrode potential**

The tendency of an electrode to gain or lose electrons when it is in contact with its own ions in solution is called electrode potential. It is denoted by 'E'.

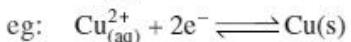
Electrode potential depends upon the

- Nature of the metal (or non-metal)
- Concentration of the electrolyte
- Temperature of the electrolyte solution
- Pressure in case of gas electrode

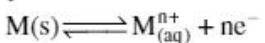
The potential of an electrode measured at standard conditions of 25°C temperature, 1 atm pressure and using ions at unit concentration is known as standard electrode potential. It is denoted by ' E° '. Standard electrode potential is also known as single electrode potential.

Potential of an electrode at 25°C , 1 atm and 1M electrolyte is called standard electrode potential

The tendency of an electrode to gain electrons or to get reduced is called its reduction potential.



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



The reduction potential of an electrode measured at 25°C, 1 atm and 1M electrolyte concentration is called standard reduction potential. For any half cell, standard reduction potential = -(standard oxidation potential)

For example, $Zn^{2+} + 2e^- \rightarrow Zn$, the standard reduction potential = - 0.76 V.

$Zn \rightarrow Zn^{2+} + 2e^-$, the standard oxidation potential = + 0.76 V.

Standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) is the primary reference electrode for measuring single electrode potential. The construction of standard hydrogen electrode is shown in Fig 4.10. SHE consists of a platinum plate dipped into a solution of protons with one molar concentration at 25°C. Hydrogen gas is passed over the Pt plate at one atm. The half cell reaction is written as, $2H^+(aq) + 2e^- \rightarrow H_2(g)$

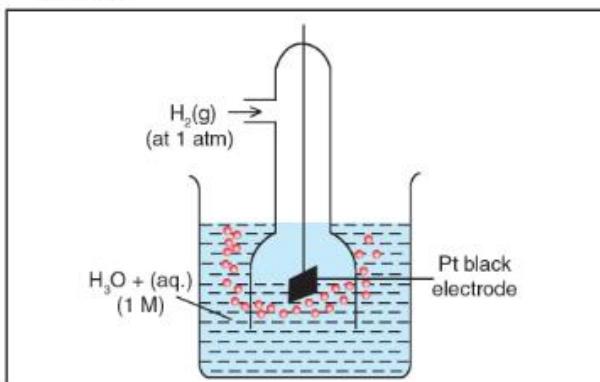


Fig 4.10 Standard hydrogen electrode

The half cell is represented as, $Pt, H^+(1M)/H_2(1\text{atm})$, $E^0 = 0.0$ volts.

Secondary reference electrodes like quinhydrone electrode and calomel electrode are also used now-a-days. Single electrode potentials are measured in a potentiometer using reference electrodes.

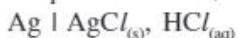
4.3.4

Metal-metal salt electrodes

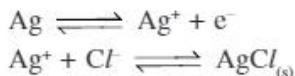
Electrodes reversible with respect to anions are also called metal-metal insoluble salt electrode.

A second type of reversible electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt.

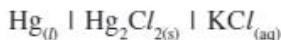
Silver-silver chloride electrode : This consists of metallic silver which is in contact with its sparingly soluble salt silver chloride. This electrode is reversible with respect to anions, i.e., Cl^- ions. This electrode may be represented as :



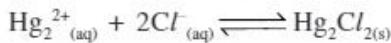
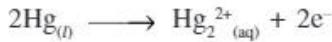
The electrode reaction involves the passage of electrode material into solution as ions and their combination with ions of the electrolyte to form insoluble salt (AgCl). Thus the sections in this type of cell are as follows :



Calomel electrode : As described earlier, the use of hydrogen electrode as a reference electrode is not always convenient in practice and therefore, several subsidiary electrodes have been devised. The most common of these is calomel electrode.



When calomel electrode involves oxidation,



When calomel electrode involves reduction,



The potential of calomel electrode depends upon the concentration of chloride ion (Commonly used KCl)

The potential of the electrode for different concentrations of KCl at 25°C are :

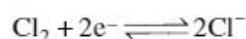
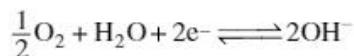
For 0.1 N KCl , $E = -0.3538$ volt

For 1.0 N KCl , $E = -0.2800$ volt

For saturated solution of KCl , $E = -0.2415$ volt

For greater accuracy, the electrode with 0.2 N KCl is preferred due to its low temperature coefficient. In some cases saturated calomel electrode is also used because it is very easy to be set up and when it is used in conjunction with a saturated potassium chloride salt bridge, the liquid junction gets avoided.

Gas Electrode : This type consists of oxygen or chlorine electrode in which oxygen or chlorine gas is bubbled through a solution of the corresponding ion. Hydroxyl or chloride ions will provide electrical contact, while using platinum.



4.3.5

Oxygen or chlorine gas is bubbled in gas electrode

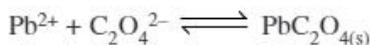
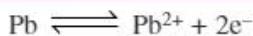
**Other type of
Electrodes**

Third type of electrode consists of a metal, one its insoluble salts, another insoluble salt of another metal having same anion and the solution of any soluble salt of the later having the same cation. An example of this type is :

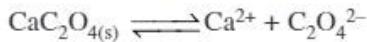


Various chemical reactions involved in this electrode are :

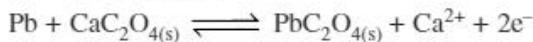
Lead first dissolves to form Pb^{2+} ions with the liberation of two electrons. The lead ions then combine with $\text{C}_2\text{O}_4^{2-}$ ions to form insoluble lead oxalate. Thus,



The removal of $\text{C}_2\text{O}_4^{2-}$ ions from the solution results in dissolving the calcium oxalate which ionises to maintain the equilibrium.



The net reaction is



The system behaves as an electrode reversible with respect to Ca^{2+} ions. This electrode is important because a reversible calcium electrode employing metallic calcium is difficult to realise experimentally.

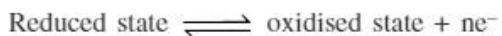
Fourth type of reversible electrodes consists of an inert electrode like platinum or gold immersed in a mixed solution containing both the oxidized and the reduced forms of a molecule or ion.

For example, Fe^{2+} and Fe^{3+} or Sn^{4+} and Sn^{2+} .

The reversible changes occurring at these electrodes involves oxidation or reduction. The electrodes and their reactions are presented as

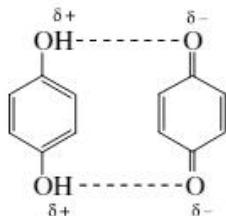


It can be shown again that the equilibrium shifts in the same direction in which the current flows. An oxidation-reduction electrode can act reversible only if ions in both oxidised and reduced states are present. It may be noted that the reaction towards the right is called oxidation since it causes liberation of electrons and towards the left is called reduction since it causes consumption of electrons. In all these cases, the electrode reactions may be written as it causes consumption of electrons. In all these cases, the electrode reactions may be written as

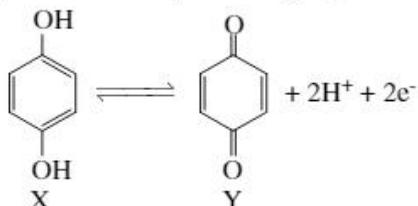


Here n is the number of electrons by which the oxidised and reduced states differ.

The equimolar mixture of quinone and hydroquinone is known as quinhydrone. Quinone and hydroquinone remains bonded with H-bond.



In aqueous solution, following equilibrium is established:



Therefore, $[X]=[Y]$ and $Q=[\text{H}^+]^2$

**Equimolar mixture
of quinone and
hydroquinone is
known as
quinhydrone**

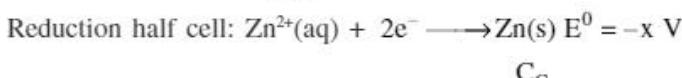
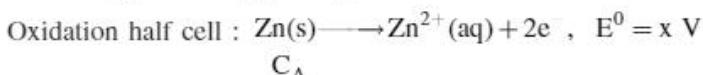
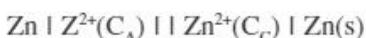
4.3.6

Concentration cell

The cells whose electrodes or half-cells are made of materials, but differ in concentration is known as concentration cell. The e.m.f. of the concentration cell is consequence of concentration difference of half-cells. In such cells,

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

For example: Consider the following concentraon cell



From Nernst equation, we get

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]_{\text{anode}}}{[\text{Zn}^{2+}]_{\text{cathode}}}$$

$$\Rightarrow E_{\text{cell}} = 0 - \frac{0.0591}{n} \log \frac{C_A}{C_C}$$

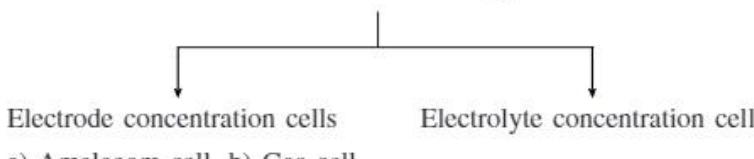
$$\Rightarrow E_{\text{cell}} = 0 + \frac{0.0591}{n} \log \frac{C_C}{C_A}$$

C_C is concentration of Zn^{2+} at cathode and C_A is concentration at anode

$$\Rightarrow E_{\text{cell}} = +\text{ve}$$

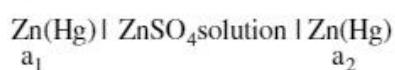
$$C_C > C_A$$

Concentration cells are classified into 2 types.

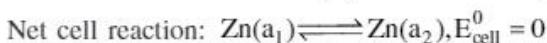
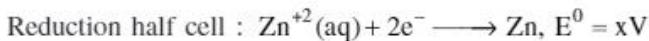



**Amalgam cell
and gas cell are
example of
electrode concen-
tration cells**


Amalgam cell : In an amalgam cell, two like electrodes of different activities are dipped in the same solutions of an electrolyte containing an ion of the electrode material.



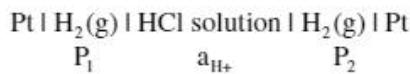
The activities of Zn in two amalgams are different.



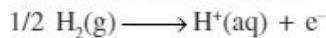
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{a_2}{a_1} = 0 - \frac{0.0591}{n} \log \frac{a_1}{a_2} = + \frac{0.0591}{n} \log \frac{a_2}{a_1}$$

Here 'n' is the number of moles of electrons exchanged.

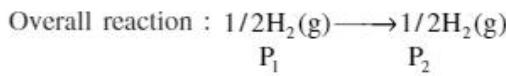
Gas cells : In gas cells, the gas electrode is generally made up of gas materials as different activities and being dipped in the solution of gas ion. The potential of such cells depends upon the pressure of gases and the concentration of their ions in solution. For example, if two hydrogen electrode at different partial pressures P_1 and P_2 are dipped in the solution of H^+ ions of activity, a_{H^+} than cell is represented as :



Oxidation half reaction :



Reduction half reaction :



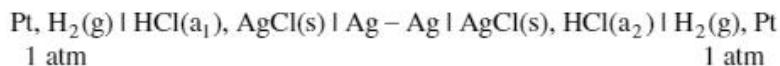
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{1} \log \left(\frac{P_2}{P_1} \right)^{1/2} = 0 + \frac{0.0591}{1} \times \frac{1}{2} \log \frac{P_1}{P_2}$$

For spontaneous reaction, $E_{\text{cell}} = +\text{ve}$. Hence, $P_2 > P_1$

*Overall reaction
of H_2 gas
electrode*
 $\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \frac{1}{2}\text{H}_2(\text{g})$
at P_1 at P_2

Electrolyte concentration cells without transference

In this type of cells, the two electrodes are made of same substance, but differs in concentrain of the reversible ions such as:



In these types of cells, there is no transfer of electrolyte from one solution to another. The half cell reactions are :



$$\text{Therefore, } E_{\text{cell}} = \frac{RT}{F} \ln \frac{a_2}{a_1}$$

4.3.7

Nernst equation

The single electrode potential (E) is related to standard reduction potential (E^0) and the concentration of the electrolyte by Nernst equation.

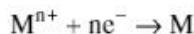
$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Oxidised form}]}{[\text{Reduced form}]} \text{ or } E = E^0 + \frac{2.303 RT}{nF} \log \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

Here n is the charge magnitude on the electrolyte, T is the absolute temperature taken as 298K and F is Faraday taken as 96500 coul. The simplified form of Nernst equation is obtained by substituting the values of respective constants.

$$E = E^0 + \frac{0.059}{n} \log \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}$$

Single electrodes are classified into two categories. The electrode whose potential is dependent on the concentration of cations or metal ions is called metal electrode. In a metal electrode, the metal ions are reversible with metal atoms. The electrode whose potential is dependent on the concentration of anions or non-metal ions is called non-metal electrode. In a non-metal electrode, the non-metal ions are reversible with non-metal atoms.

Metal electrodes: In the metal electrode, M^{n+} cation is the oxidised form and metal atom, M is the reduced form. The electrode reaction is given as

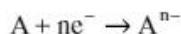


Taking the concentration of M^{n+} in solutions as 'C' and the active mass of M as 1, the Nernst equation is written as,

$$E = E^o + \frac{2.303 RT}{nF} \log C \quad (\text{or}) \quad E = E^o + \frac{0.059}{n} \log C$$

Hydrogen electrode is considered as metal electrode, since metal electrode involves the reduction of cations.

Non-metal electrodes: In the non-metal electrode, the non-metal atom A is reduced to A^{n-} anion. The electrode reaction is given as



Taking the active mass of A as 1 and the concentration of A^{n-} in solutions as 'C', the Nernst equation is written as,

$$E = E^o - \frac{2.303 RT}{nF} \log C \quad (\text{or}) \quad E = E^o - \frac{0.059}{n} \log C.$$

Upon dilution of the electrolyte, the reduction potential of a metallic electrode decreases and a non-metallic electrode increases. Concentration dependence of reduction potentials of copper and chlorine electrode is recorded in [Table 4.7](#).

Table 4.7 Reduction potentials with different electrolyte concentrations

Concentration of $CuSO_4$	Potential of Cu^{2+}, Cu	Concentration of HCl	Potential of Pt, Cl_2, Cl^-
1.0 M	0.34 V	1.0 M	1.36 V
0.1 M	0.281 V	0.1 M	1.419 V
0.01 M	0.222 V	0.01 M	1.478 V
0.001 M	0.163 V	0.001 M	1.537 V
0.0001 M	0.1335 V	0.0001 M	1.596 V

4.3.8

Electrochemical series

The arrangement of electrodes in the order of increasing reduction potentials is called electrochemical series. This is also called activity series.

The negative sign of standard reduction potential indicates that when the electrode is connected with standard hydrogen electrode, it acts as the anode and oxidation takes place. A positive sign of standard reduction potential indicates that the electrode acts as cathode when connected with a standard hydrogen electrode. The activity series containing important half-cells are listed in [Table 4.8](#).

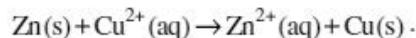
Table 4.8 Electrochemical series

	Half cell reaction	Electrode	E° (volts)
↑ Oxidising strength	$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	Li^+ / Li	- 3.05
	$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	K^+ / K	- 2.93
	$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	$\text{Ca}^{2+} / \text{Ca}$	- 2.87
	$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	Na^+ / Na	- 2.71
	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	$\text{Mg}^{2+} / \text{Mg}$	- 2.37
	$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	$\text{Al}^{3+} / \text{Al}$	- 1.66
	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	$\text{Pt}, \text{H}_2\text{O}/\text{OH}^-$	- 0.83
	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	$\text{Zn}^{2+} / \text{Zn}$	- 0.76
	$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	$\text{Cr}^{3+} / \text{Cr}$	- 0.74
	$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	$\text{Fe}^{2+} / \text{Fe}$	- 0.44
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	$\text{Ni}^{2+} / \text{Ni}$	- 0.25
	$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	$\text{Sn}^{2+} / \text{Sn}$	- 0.14
	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	$\text{Pb}^{2+} / \text{Pb}$	- 0.13
	$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	$\text{Pt}, \text{H}^+ / \text{H}_2$	0.00
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	$\text{Cu}^{2+} / \text{Cu}$	+ 0.34
	$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	$\text{Pt}, \text{I}_2 / \text{I}^-$	+ 0.54
	$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	$\text{Pt}, \text{O}_2 / \text{H}_2\text{O}_2$	+ 0.68
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	$\text{Fe}^{3+} / \text{Fe}^{2+}$	+ 0.77
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	Ag^+ / Ag	+ 0.80
↓ Reducing strength	$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	Hg^+ / Hg	+ 0.85
	$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-(\text{aq})$	$\text{Pt}, \text{Br}_2 / \text{Br}^-$	+ 1.07
	$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	$\text{Pt}, \text{O}_2 / \text{H}_2\text{O}$	+ 1.23
	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 6\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$\text{Pt}, \text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+}$	+ 1.33
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	$\text{Pt}, \text{Cl}_2 / \text{Cl}^-$	+ 1.36
	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	$\text{Au}^{3+} / \text{Au}$	+ 1.40
	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$\text{Pt}, \text{MnO}_4^- / \text{Mn}^{2+}$	+ 1.51
	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	$\text{Pt}, \text{H}_2\text{O}_2 / \text{H}_2\text{O}$	+ 1.77
	$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	$\text{Pt}, \text{O}_3 / \text{O}_2$	+ 2.07
	$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	$\text{Pt}, \text{F}_2 / \text{F}^-$	+ 2.87

Applications of activity series

Chemical reactivity of metals: The metal which has high negative value of standard reduction potential readily loses electrons and it is converted into cation. Such a metal is said to be chemically very active. The chemical reactivity of metals decreases from top to bottom in the activity series.

In the Daniell cell the net reaction is given as,



Zn ($E^\circ = - 0.76$ volts) is more active and displaces Cu^{+2} ion ($E^\circ = 0.34$ volts).


Oxidation ability increases with increase in the reaction potential



Metals with negative SRP liberate H₂ with mineral acids

EMF of cell is the difference in potentials of cathode and anode


Relative strength of oxidising and reducing agents: The reducing ability decreases from top to bottom in the electrochemical series. The oxidation ability increases with increase in the reduction potential.

$$\text{Oxidising power} \propto \text{reduction potential} \propto \frac{1}{\text{oxidation potential}}$$

$$\text{Reducing power} \propto \text{oxidation potential} \propto \frac{1}{\text{reduction potential}}$$

Fluorine with highest reduction potential is the best oxidant. Lithium with least reduction potential is the best reductant in aqueous medium based on the potentials.

A given metal in activity series can reduce all the metal ions present below it and oxidise all metal atoms present above it. A metal can reduce all the non-metals present below it in the activity series.

A non-metal can oxidise all metal atoms present above it in the activity series. It can also oxidise non-metal anions present above it.

Displacement of hydrogen from dilute acids by metals: The metals accompanying top positions in the electrochemical series readily liberate hydrogen from dilute acids. On descending in the series, tendency to liberate hydrogen gas from dilute acids decreases. The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, Ag, etc., do not evolve hydrogen from dilute acids.

Calculation of EMF of cell: From the standard reduction potentials of electrochemical series, we can find out the EMF of the cell.

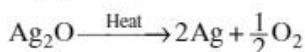
$$\text{EMF of the cell (or)} E_{\text{cell}} = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$\text{eg: } E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ volts and } E_{\text{Ag}^+/\text{Ag}}^0 = +0.8 \text{ volts}$$

The notation of the cell is, Zn/Zn²⁺ // Ag⁺/Ag

$$E_{\text{cell}}^0 = +0.8 - (-0.76) = +1.56 \text{ volts}$$

Thermal stability of metallic oxides : The thermal stability of metal oxides decreases from top to bottom in the electrochemical series.



Products of electrolysis: In case two or more types of positive ions are present in solution, the ion which has high value of standard reduction potential is discharged at the electrode in preference to other ions.

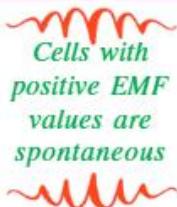
Spontaneity of reaction: In the galvanic cells, the free energy change or Gibbs energy change ($-\Delta G$) of the redox reaction is converted into electrical energy. In the electrochemical cell electromotive force is equal to the free energy change. It is given as,

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

Here n is the number of electrons transferred in the redox reaction and F is the Faraday constant.

If the substances involved in the redox reaction of the cell are all in standard states, the standard Gibbs energy change (ΔG^0) is equal to nFE_{cell}^0 .

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



Cells with positive cell potentials are spontaneous, since the Gibbs energy change is negative. For such cells, equilibrium constants of redox reactions are high.

For the reversible cell reaction, $aA + bB \rightleftharpoons mP + nQ$, the equilibrium constant,

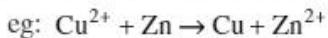
$$K = [P]^m [Q]^n / [A]^a [B]^b$$

$$\Delta G = \Delta G^{\circ} + RT \ln K$$

Substituting the values, $-\Delta G = nFE_{\text{cell}}$ and $-\Delta G^{\circ} = nFE_{\text{cell}}^{\circ}$,

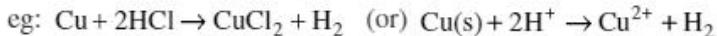
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln K \quad (\text{or}) \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log K$$

A redox reaction is feasible if the electrode having higher reduction potential is reduced and the electrode having lower reduction potential is oxidised. Otherwise redox reaction is not feasible.



$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = +0.34 - (-0.76) = 1.1 \text{ volts}$$

So the redox reaction is possible.



$$E_{\text{cell}}^{\circ} = 0.0 - 0.34 = -0.34 \text{ volts}$$

So the redox reaction is not normally possible.



- P.4.20** E° of zinc electrode is -0.762V . Calculate the single electrode potential of Zn electrode in decimolar ZnSO_4 solution.

Solution Simplified Nernst equation for single electrode potential,

$$E = E^{\circ} + \frac{0.059}{n} \log C \quad (\text{or}) \quad E = E^{\circ} + \frac{0.059}{2} \log [\text{Zn}^{2+}]$$

Substituting the values in the expression for the single electrode potential of Zn,
 $E = -0.762 + 0.0295 \log 10^{-1} = -0.7915\text{V}$.



- P.4.21** At what concentration of copper sulphate solution, the potential of $\text{Cu}^{2+}, \text{Cu}$ becomes zero? The standard reduction potential of $\text{Cu}^{2+}, \text{Cu}$ is 0.34V .

Solution $E = E^{\circ} + \frac{0.059}{n} \log C \quad (\text{or}) \quad 0 = 0.34 + \frac{0.059}{2} \log [\text{Cu}^{2+}]$

$$0.0295 \log [\text{Cu}^{2+}] = -0.34 \quad (\text{or}) \quad \log [\text{Cu}^{2+}] = -\frac{0.34}{0.0295} = -11.57$$

$$\text{Concentration of CuSO}_4 = 10^{-11.57} = 10^{-12+0.43} = 2.9 \times 10^{-12} \text{ M.}$$



- P.4.22** At 25°C , the reduction potential of hydrogen electrode is -0.118 V at 1 atm. What is the pH of acid solution used for the construction of the electrode?

Solution $E = E^{\circ} + \frac{0.059}{n} \log C \quad (\text{or}) \quad E = E^{\circ} + \frac{0.059}{2} \log [\text{H}^+]$

$$-0.118 = 0.059 \log [\text{H}^+] \quad (\text{or}) \quad -\log [\text{H}^+] = 2 ; \text{ pH} = 2.$$



- P.4.23** A cell is constructed using $\text{Pb}^{2+}, \text{Pb}$ and $\text{Ni}^{2+}, \text{Ni}$ electrodes. If E° values of Pb and Ni electrodes are respectively -0.13 and -0.25V , write (a) the cell reaction and (b) cell notation.

Solution Reduction potential of Ni electrode is less and hence it reduces Pb^{2+} ions.

The cell reaction is written as, $\text{Ni} + \text{Pb}^{2+} \rightarrow \text{Pb} + \text{Ni}^{2+}$

The oxidation half reaction is, $\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$

The reduction half reaction is, $\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$

The cell is written as, $\text{Ni, Ni}^{2+}(\text{aq}) // \text{Pb}^{2+}(\text{aq}), \text{Pb}$.



P.4.24 E° values of N^{2+} , Ni and Cl_2 , Cl^- are respectively -0.25V and $+1.37\text{V}$. Calculate the EMF of the cell $Ni, Ni^{2+} (0.01\text{M}) // Cl^- (0.1\text{M}), Cl_2, Pt$.

Solution Potential of nickel electrode is given as,

$$E = E^\circ + 0.0295 \log [Ni^{2+}] = -0.25 + 0.0295 \log 10^{-2} = -0.25 + 0.0295(-2) = -0.305\text{V}$$

Potential of chlorine electrode is given as,

$$E = E^\circ - 0.059 \log [Cl^-] = +1.37 - 0.059 \log 10^{-1} = 1.43\text{V}$$

$$\text{EMF of cell} = E(\text{chlorine electrode}) - E(\text{nickel electrode}) = 1.43 - (-0.305) = 1.735\text{ V.}$$



P.4.25 Lithium is the strongest reductant in aqueous solutions. Why?

Solution Standard potential for the reaction $Li^+(aq) + e^- \rightarrow Li(s)$ is -3.05V . It is least among all reduction potentials. This is because of high stability of aqueous lithium cation due to greater hydration. Smaller the reduction potential greater is the reduction ability of the metal.



P.4.26 Calculate the standard Gibbs energy change for the redox reaction of Daniell cell.

Solution Cell reaction in Daniell cell is $Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$

The standard electrode potential, E_{cell}° is 1.1V .

$$\text{The standard free energy change, } \Delta G^\circ = -nFE_{cell}^\circ = -2 \times 1.1 \times 96500 = -21.3\text{ kJ mol}^{-1}.$$



P.4.27 Mention electrodes and write the cell representing a redox reaction, $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$.

Solution Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2 . Zinc electrode is anode and hydrogen electrode is cathode. The cell is represented as, $Zn, Zn^{2+}(aq) // H^+(aq), H_2, Pt$.



P.4.28 Calculate the solubility product of Ag_2CrO_4 at $298K$, if the EMF of the concentration cell, $Ag, Ag^+(\text{solid } Ag_2CrO_4) // Ag^+(0.1\text{M}), Ag$ is 0.164V .

Solution $E_{cell} = 0.164 = 0.059 \log [Ag^+]_{cath} / [Ag^+]_{anod}$

$$\log \frac{[Ag^+]_{cath}}{[Ag^+]_{anod}} = \frac{0.164}{0.059} = 2.78 = \log \frac{0.1}{[Ag^+]_{anod}}$$

$$[Ag^+]_{anod} = [Ag^+] \text{ from saturated solution of } Ag_2CrO_4 = 1.66 \times 10^{-4}\text{M}$$

$$\text{Solubility product of } Ag_2CrO_4 \text{ is given as, } [Ag^+]^2 [CrO_4^{2-}]$$

$$\text{Solubility product of } Ag_2CrO_4 = (1.66 \times 10^{-4})^2 (1.66 \times 10^{-4} / 2) = 2.28 \times 10^{-12} \text{ mol}^3 \text{ lit}^{-3}.$$



P.4.29 $Mg(s) + 2Ag^+(0.0001\text{M}) \rightarrow 2Ag(s) + Mg^{2+}(0.13\text{M})$. Calculate the E_{cell} if E_{cell}° is given as 3.17V .

Solution E_{cell} is written directly from E_{cell}° as,

$$E_{cell} = E_{cell}^\circ - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^+]^2} \quad (\text{or}) \quad E_{cell} = 3.17 - \frac{0.059}{2} \log \frac{0.13}{(0.0001)^2}$$

$$E_{cell} \text{ of the given reaction} = 3.17 - 0.21 = 2.96\text{ V.}$$



P.4.30 E_{cell}° for the redox reaction $2Ag^+(aq) + Cu \rightarrow Cu^{2+}(aq) + 2Ag$ is 0.46V . Calculate the equilibrium constant of the reaction.

Solution E_{cell}° for the given reaction $= \frac{0.059}{2} \log K = 0.46\text{V}$ (or) $\log K = \frac{0.46 \times 2}{0.059} = 15.6$

$$\text{Equilibrium constant, } K = 10^{15.6} = 3.9 \times 10^{15}.$$

EXERCISE - 4.1.3

- How is electrical energy generated by performing a chemical reaction?
- Describe the construction and working of Daniell cell.
- What is single electrode potential? How is it dependent on various factors?
- Write the Nernst equation for a metal electrode and for a non-metal electrode.
- Describe the construction of standard hydrogen electrode.

6. What is electrochemical series? Write different applications of the series.
7. How are the cells systematically represented? Give examples.
8. $E_{\text{Ag}^+, \text{Ag}}^0 = 0.8\text{V}$. Calculate the single electrode potential in 0.01M Ag^+ .
(Ans : 0.682V)
9. E^0 values of Zn^{2+} , Zn and Cu^{2+} , Cu are respectively -0.76V and $+0.34\text{ V}$. Calculate the EMF of the cell $\text{Zn}/\text{Zn}^{2+}(0.1\text{M})/\text//\text{Cu}^{2+}(0.1\text{M})/\text{Cu}$.
(Ans : 1.1 V)
10. The potential of the cell $\text{Cu}, \text{Cu}^{2+}(0.1\text{M})/\text//\text{HCl (xM)}, \text{Cl}_2, \text{Pt}$ is 1.07V . If the standard potentials of copper and chlorine electrodes are 0.34V and 1.36V , calculate the concentration of HCl.
(Ans : 0.01M)
11. Represent the cell in which the following reaction takes place
 $\text{Mg(s)} + 2\text{Ag}^+(0.001\text{ M}) \rightarrow \text{Mg}^{2+}(0.130\text{ M}) + 2\text{Ag(s)}$. Calculate its $E_{\text{(cell)}}$ if $E_{\text{(cell)}}^- = 3.17\text{ V}$
(Ans : 2.96 V)
12. E^0 values of Co^{2+} , Co ; Al^{3+} , Al ; Ag^+ , Ag and Ba^{2+} , Ba are respectively -0.28 , -1.66 , $+ 0.8$ and -2.9V . Write the increasing order of the reduction ability of metals and discuss.
(Ans : $\text{Ag} < \text{Co} < \text{Al} < \text{Ba}$)
13. E^0 for $\text{Mg} \rightarrow 2\text{e}^- + \text{Mg}^{2+}$ is $+2.37\text{V}$ and for $\text{Cu} \rightarrow 2\text{e}^- + \text{Cu}^{2+}$ is -0.34V . What will be the standard potential of cell constructed with these electrodes? Which electrode will be positive terminal to draw the current?
(Ans : 2.71V, Cu electrode)
14. Standard reduction potentials of I_3^-, I^- and Fe^{3+} , Fe^{2+} are 0.54 and 0.77V , respectively. Calculate the equilibrium constant for the reaction, $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$.
(Ans : 6.25×10^7)
15. Two students use the same stock solutions of zinc sulphate and a solution of copper sulphate. The EMF of one cell is 0.0295V higher than the other. The concentration of cupric ions used in the cell with higher EMF value is 0.2M . Calculate the concentration of cupric ions used in the other cell.
(Ans : 0.02M)
16. Calculate the equilibrium constant of the reaction.
 $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$; $E_{\text{(cell)}}^- = 0.46\text{ V}$
(Ans : 3.9×10^{15})
17. The standard electrode potential for Daniell cell is 1.1 V . Calculate the standard Gibbs energy for the reaction : $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
(Ans : $-212.3\text{ kJ mol}^{-1}$)

OTHER CELLS

Battery is an example of electrochemical cell. It consists of two or more voltaic cells connected in series. The voltage of a battery should not vary much during its use. Mainly two types of cells are used : primary cells and secondary cells.

4.4.1

Primary cells

Every voltaic cell, in a most general sense, is a primary cell. But cells which can function as practical useful sources of current are termed as primary cells. A primary cell is not rechargeable.

Primary cell is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current. In the primary cells, reaction occurs only once and cannot be reused

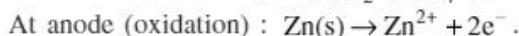
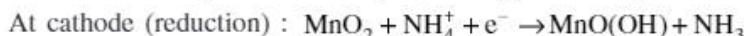
Primary cell is a source of energy without being previously charged

The potential of Lechlanche cell is nearly 1.5 V

The potential of mercury cell is nearly 1.35 V

again because they become dead over a period of time. The most familiar example of primary cell is the dry cell. It is a Lechlanche cell, in which the electrolytic solution is replaced by electrolyte paste. Dry cell is used in clocks, transistors and torches.

Dry cell consists of a zinc container which acts as anode and graphite as cathode rod surrounded by powdered manganese dioxide and carbon as shown in Fig 4.11. The space between electrodes is filled by a moist paste of ammonium chloride. The reactions occur in dry cell are complex, but approximately shown as,



Ammonia produced in the reaction forms a complex compound, $[\text{Zn}(\text{NH}_3)_4]\text{Cl}_2$. The potential of the dry cell is nearly 1.5V. In dry cell, MnO_2 acts as cathodic depolarises and facilitate the H^+ ion discharge reaction by removing the absorbed hydrogen atoms.

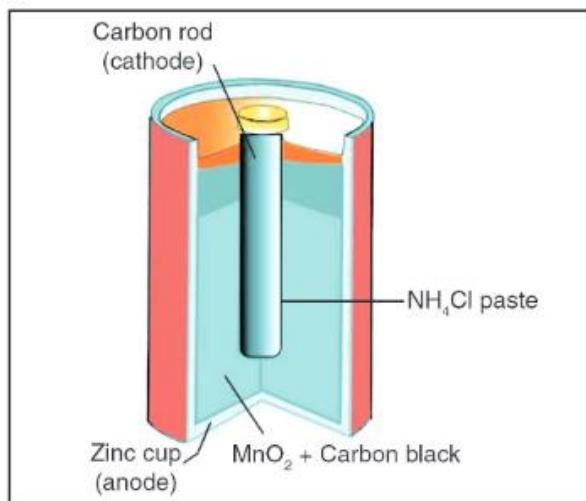
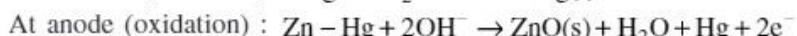


Fig 4.11 Common dry cell

Mercury cell (Fig 4.12) is another dry cell suitable for low current devices. It consists of a paste of potash and zinc oxide acting as electrolyte. A paste of carbon and mercuric oxide acts as cathode and zinc amalgam as anode. The electrode reactions are,



The overall reaction is, $\text{Zn} - \text{Hg} + \text{HgO(s)} \rightarrow \text{ZnO(s)} + 2\text{Hg(l)}$.

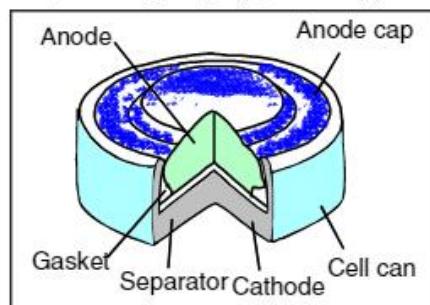


Fig 4.12 Mercury dry cell

This cell does not involve any ion, whose concentration changes during its life time. Potential of mercury dry cell is approximately 1.35V.

4.4.2

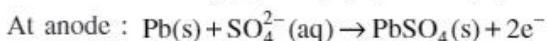
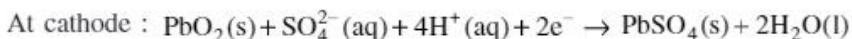
Secondary cells


Lead accumulator is a reversible galvanic cell used as storage battery


Secondary cell is one in which electrical energy from an external source is first converted into chemical energy. When external source is removed, the cell is made to operate in the reverse direction. Storage battery is a secondary cell. There will be process of charging and discharging which are mutually reversible chemical reactions occurring in the cell.

Theoretically a reversible galvanic cell should be able to store electrical energy. But most of them are practically unsuitable because of low energy storing capacity and incomplete reversibility. Most common reversible storage cell is lead accumulator (Fig 4.13), used in inverters and automobile vehicles. It is called acid storage cell and represented as: $\text{Pb}, \text{H}_2\text{SO}_4, \text{PbO}_2$. Alkali storage cell is called Edison battery.

Lead storage battery consists of two lead electrodes, both are reversible. Sponge lead is used as anode and a grid of lead packed with plumbic oxide as cathode. A 38% aqueous solution of sulphuric acid is used as electrolyte. When the battery is in use, the cell reactions are:



The overall cell reaction is:

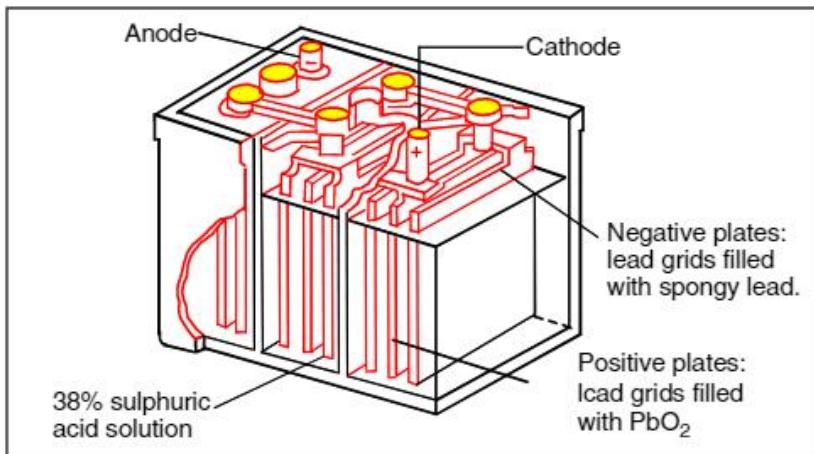
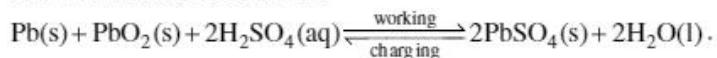


Fig 4.13 Lead storage battery

On charging the battery, the electrode reactions are reversed. Lead sulphate accumulated on cathode and anode is converted into lead and lead dioxide respectively. Charging and discharging of lead storage battery is known as double sulphonation.

The voltage of the battery increases with the concentration of electrolyte. The voltage varies from 1.88V (5% H_2SO_4) to 2.15V (40% H_2SO_4).

Another important secondary cell is nickel–cadmium cell (Fig 4.14). This is more expensive to manufacturer, but has longer life than lead storage battery. The overall reaction during discharge of nickel–cadmium cell is given as,



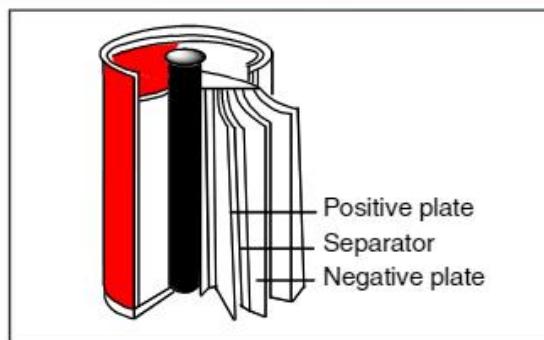


Fig 4.14 A rechargeable nickel-cadmium Cell

4.4.3**Fuel cells**


Fuel cell is a galvanic cell designed to convert combustion energy into electrical energy


In thermal power plants, the chemical energy of fossil fuels such as coal, oil, gas or wood is first used for converting water into high pressure steam. Steam is then used to run a turbine to produce electricity. Production of electricity by thermal plants is a major source of pollution and suffers with lower efficiency.

A galvanic cell directly converts chemical energy into electrical energy and the efficiency is high. Galvanic cells that are designed to convert combustion energy directly into electrical energy are called fuel cells.

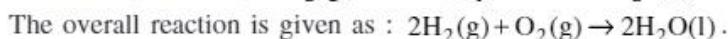
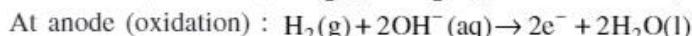
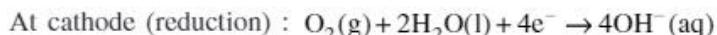
The fuel cell also has two electrodes and one electrolyte. The fuel is oxidised at anode and oxidant is reduced at cathode. Fuel and oxidant are continuously and separately supplied by the two electrodes of the cell at which they undergo reaction. Fuel cells are primary cells and are capable of supplying current as long as they are provided with fuel and oxidant. A fuel cell is represented as:

Fuel / Anode / Electrolyte / Cathode / Oxidant.

The useful fuels are hydrogen, methane, carbon monoxide, methanol, hydrazine, etc. The oxidants used are: oxygen, air, hydrogen peroxide, ozone, nitric acid, etc. The electrodes used are: Porous carbon or platinum, polyvinyl chloride or teflon coated with silver, raney nickel, nickel oxide, etc. Catalysts are also used in fuel cells. Organic compounds are disintegrated by micro organisms in biochemical fuel cells.

Fuel cells are classified into three types, based on the temperature of operation: below 100°C are low temperature cells, between 100 – 300°C are medium temperature cells and above 400°C are high temperature cells.

Hydrogen–oxygen, as shown in Fig 4.15 fuel cell consists of porous electrodes suspended in concentrated caustic soda solution. Fuel and oxidant gases are bubbled at the surface of porous carbon electrodes embedded with suitable catalysts. The electrode reactions are,



The heat of combustion is directly converted into electrical energy. The efficiency of energy conversion in fuel cells is generally more than 70%.

Methane–oxygen fuel cell consists of platinum electrodes suspended in phosphoric acid, which acts as electrolyte.


Hydrogen-oxygen fuel cell consists of two porous electrodes and NaOH solution as electrolyte



*Efficiency of
energy
conversion in
fuel cells is
more than 70%*

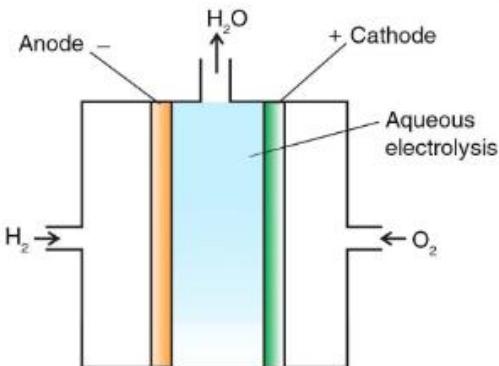



Fig 4.15 Hydrogen-Oxygen fuel cell

Fuel cells are now used in automobiles on an experimental basis. Fuel cells have silent operation, high efficiency and are free from pollution. The absence of moving parts in fuel cells eliminates wear and tear problems. They were used as power sources in space crafts Gemini and Apollo. The water formed in hydrogen–oxygen cell is pure and hence used for drinking purpose in space ships.



P.4.31 Second law of thermodynamics is not a restriction in the working of a fuel cell. Explain.

Solution Conventional method of converting chemical energy into electrical energy involves three steps.

Step I : Chemical energy \longrightarrow Heat energy

Step II : Heat energy \longrightarrow Mechanical energy

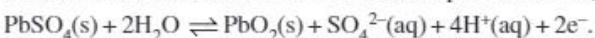
Step III : Mechanical energy \longrightarrow Electrical energy

The extent of heat converted into mechanical energy (step II) is limited by the second law of thermodynamics. Hence, the power plants are with only 40% efficiency. But in a fuel cell, chemical energy is directly converted into electrical energy, with a theoretical 100% efficiency.



P.4.32 What happens when lead storage battery is subjected to charging?

Solution Charging of storage battery is the reverse of its discharge. The lead sulphate deposited on electrodes is reduced to lead and oxidised to plumbic oxide, with a net reaction for two faradays.



The cell potential increases during charging. Hence, lead storage battery can be reused.



P.4.33 Potash solution is not recommended in a hydrocarbon–oxygen fuel cell. Why?

Solution The combustion products of a hydrocarbon are CO_2 and H_2O . CO_2 is a non-metallic oxide and acidic. It is absorbed in the electrolyte if KOH is used. To avoid this, phosphoric acid is used as electrolyte in hydrocarbon–oxygen fuel cell.



P.4.34 What are the limitations of fuel cells?

Solution Fuel cell is a primary cell. It can not be used as storage cell. Moreover, catalysts used in the fuel cell are costly and gaseous fuels are difficult to store. Caustic soda as electrolyte is corrosive.

EXERCISE - 4.1.4

1. Distinguish between primary and secondary cells used as batteries.
2. Write the construction and working of dry cell.
3. Explain the functions of lead accumulator.
4. Discuss the working of hydrogen–oxygen fuel cell. What are the advantages of using this fuel cell?

CORROSION

Active metals naturally occur as their compounds such as oxides, sulphides, sulphates, carbonates and silicates. Metals are extracted from these compounds. But metals look forward for favourable conditions to convert back to the stable compounds from which they are extracted.

4.5.1

Corrosion

Conversion of metal into its mineral in environment is called corrosion

Anodic dissolution of metal is electrochemical corrosion

Natural tendency of conversion of a metal into its mineral compound on interaction with environment is known as corrosion. Rusting of iron, tarnishing of silver and development of green coating on copper alloys are some important examples of corrosion. Metallic corrosion causes enormous damage to bridges, buildings, ships, etc.

Process of corrosion may be chemical or electrochemical. Electrochemical corrosion is considered as the anodic dissolution of metal undergoing corrosion. Anodic dissolution involves oxidation of metal.



Electrochemical corrosion occurs if the environmental conditions of metal favour the formation of a galvanic cell with the metal acting as anode. The dissolution of metal may be hydrogen evolution type or differential oxygenation type.

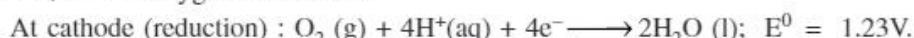
Hydrogen evolution type corrosion is exhibited by metals with negative reduction potentials. These metals displace hydrogen from aqueous solutions. Potential of hydrogen electrode is zero in one molar acid solutions on Pt cathode. It is $-0.8V$ on Hg cathode. The anodic corrosion of the metal depends upon pH of aqueous solutions, nature of anode metal and impure metal present as cathode. Pure zinc does not corrode in salt solutions but corrodes in the presence of copper impurity. Zinc does not corrode in neutral salt but corrodes in 2M acid solution.

If oxygen is not uniformly distributed on the surface of the metal, metal corrodes at those points where concentration of oxygen is less. The portion of metal with access to high concentration of oxygen functions as cathode and with low oxygen as anode. Metal with differential oxygenation, functions as galvanic cell. The portion of metal access to lower oxygen concentration acts as anode and undergoes anodic dissolution.

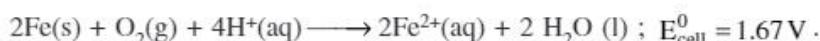
Rusting of iron is a common example of differential oxygenation type corrosion. The mechanism of corrosion is quite complex. At a particular spot of object of iron, it behaves as anode, oxidation takes place and metal dissolves.



Electrons released at anodic spot of iron move through the metal, go to another spot and reduce oxygen in the presence of proton. The spot of iron behaves as cathode, where oxygen is reduced.



The overall reaction is:



**Chemically rust
is hydrated ferric
hydroxide**

Since E_{cell} is positive, the free energy change is negative, suggesting the corrosion is spontaneous. Further, ferrous is oxidised to ferric in the atmospheric oxygen and forms rust. Rusting of iron in atmosphere is shown in Fig 4.16. Rust is chemically hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

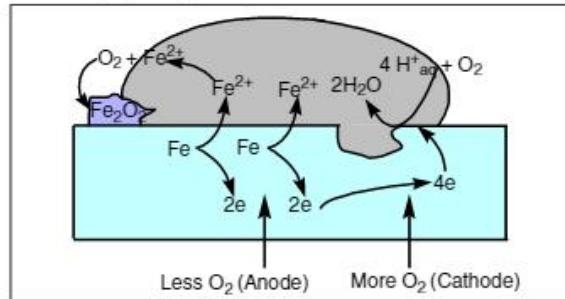


Fig 4.16 Rusting of iron in atmosphere

**Corrosion is
presented by
separating metal
from environment**

The main principle underlying the method of prevention of corrosion is to separate the metal from the environment. Some of the methods are :

1. Painting the metal object protects the surface of the metal from the impact of environment.
2. Prevention of metal surface from electrical conducting media.
3. Alloying the metal with more anodic metal.

Iron pole in sea water undergoes corrosion faster, than iron on beach, because iron in sea water suffers with high salt concentration. Iron immersed in aqueous solution gets corroded as the available oxygen concentration is less. Corrosion of galvanised iron is less than iron, because in galvanisation, more anodic metal zinc is used to prevent rusting of iron.

If a metal passes another metal impurity which is present below than itself in electrochemical series, then the metal will be corroded easily, as impurity behaves as cathode and metal behaves as anode.



P.4.35 Highly conducting solutions favour rapid corrosion. Explain.

Solution Corrosion generally involves oxidation of metal. If metal is in contact with high ionic concentrations, it favours oxidation. Atmospheric corrosion resulting from exposure of a metal to air generally contains water vapour, H_2S , CO_2 , SO_2 , etc. These materials are responsible for electrochemical corrosion.



P.4.36 A long iron rod is partially dipped in common salt solution. What happens?

Solution The part of iron rod dipped in salt solution has less access to atmospheric oxygen. The concentration of oxygen is less on that part of metal. The immersed part is corroded and the process is called anodic dissolution.



P.4.37 Concentrated nitric acid can be transported in vessels of iron. Why?

Solution Iron metal is passive to concentrated nitric acid.

When Al vessel is filled with con. HNO_3 , a protective oxide film of Fe_2O_3 is formed. This film prevents further reactions of acid with metal. Hence HNO_3 can be transported in iron cans.

EXERCISE - 4.1.5

1. What is corrosion? Discuss the methods for preventing corrosion.
2. Discuss on the hydrogen evolution type corrosion of metals.
3. Discuss the process of rusting of iron.



1. The branch of science that deals with the interconversion of chemical and electrical energies is called electrochemistry.
2. Substance that does not allow electric current to pass through it is called insulator or non-conductor.
3. Substance that allows electric current to pass through it is called electric conductor.
4. Conduction through metal is due to movement of free electrons. Conduction through electrolytes is due to the mobility of free ions.
5. The reciprocal of resistance is called conductivity. Specific conductance is the reciprocal of resistivity.
6. Kohlrausch law of independent migration states that the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of equivalent conductivities of ions at infinite dilution of electrolyte.
7. Substances which allow the passage of electricity through their fused state or aqueous state and undergo chemical decomposition are called electrolytes.
8. Electrolysis is the process of decomposition of a substance by passing electricity through its aqueous state or its fused state.
9. During electrolysis oxidation occurs at anode and reduction at cathode.
10. Theory of electrolytic dissociation is due to Arrhenius and laws of electrolysis are by Faraday.
11. Faraday's first law : the amount of a substance liberated at an electrode is directly proportional to the quantity of electricity passed through it.
12. Faraday's second law : the amounts of different substances liberated at the respective electrodes using the same quantity of electricity are directly proportional to their equivalent weights.
13. The amount of substance deposited by passing one coulomb of current is called electrochemical equivalent.
14. Faraday is the quantity of electricity required to liberate one gram equivalent weight of a substance.
15. Faraday is the charge on one mole of electrons which is given as 96,500 coulombs.
16. Device in which chemical energy is converted into electricity is called galvanic cell or voltaic cell.
17. A galvanic cell is generally represented as: $\text{Zn} / \text{Zn}^{2+}(\text{aq}) // \text{Cu}^{2+}(\text{aq}) / \text{Cu}$.
18. The tendency of an electrode to gain or to lose electrons when it is in contact with its own ions is called electrode potential.

19. Electromotive force of a cell is given as, $\text{EMF} = E_{\text{cathode}} - E_{\text{anode}}$.
20. Electrode potential depends upon nature of the metal, concentration of the electrolyte, temperature and pressure.
21. The single electrode potential is calculated using Nernst equation. Potential of metal electrode (E) is related to its standard potential (E^0) as, $E = E^0 + (2.303 \frac{RT}{nF}) \log[M^{n+}]$
22. The arrangement of electrodes in the order of increasing reduction potentials is called electrochemical series.
23. Primary cell is an electrochemical cell which acts as a source of electrical energy without being previously charged up by electric current.
24. Lead accumulator is reversible cell, which can be charged and recharged. It is a secondary cell.
25. A galvanic cell designed to convert combustion energy directly into electricity is called fuel cell.
26. Natural tendency of conversion of metal into its mineral compound in environment is called corrosion. Electrochemical corrosion is anodic dissolution of metal.
27. Rust is chemically hydrated ferric oxide and is denoted as, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

EXERCISE - 4.2

1. Distinguish between strong electrolytes, weak electrolytes and non-electrolytes.
2. Define conductance, specific conductance, molar conductivity and equivalent conductivity. Discuss.
3. Write Debye–Hückel–Onsager equation. Based on the equation how is the equivalent conductance at infinite dilution calculated?
4. Equivalent conductance of a weak electrolyte at infinite dilution cannot be directly measured. Why? How is this calculated?
5. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.
(Ans : $2.3 \times 10^{-2} \text{ Sm}^2 \text{ mol}^{-1}$)
6. Passage of charge through aqueous CuSO_4 in the presence of Pt electrodes increases its pH value. Explain.
7. Discuss the electrolysis products of (a) fused NaCl and (b) aqueous NaCl at Pt electrodes.
8. Write the difference in the electrolysis of dilute sulphuric acid and 50% sulphuric acid at Pt electrodes.
9. Define and discuss electrochemical equivalent and chemical equivalent.
10. Write on the techniques, electroplating and electrotyping.
11. What are the main differences between electromotive force of cells and cell potential?
12. Write the IUPAC notations of representing cathode, anode and galvanic cell.

CHEMISTRY IID

13. What are reference electrodes? How is a secondary reference electrode used in measuring electrode potentials?
14. Calculate the time required for a current of 2 amp to decompose one gram mole of water.
(Ans : 53.6 hr)
15. An electric current is passed through two solutions (a) AgNO_3 and (b) a solution of 10g of blue vitriol in 500 ml water, using Pt electrodes separately. After 30 min, it was found 1.307 g Ag was deposited. What was the concentration of Cu^{2+} after electrolysis ? (Ans : 4.327 g L^{-1})
16. A current of 1.7 amp is passed through 300 ML of 0.16 M ZnSO_4 solution for 230 s with a current efficiency of 90%. Find the concentration of divalent zinc in solution. (Ans : 0.154 M)
17. A 200 W, 110 V in candescent lamp is connected in series with cell containing aqueous ZnCl_2 solution. What is the time required to deposit 1.109 g of metal ?
(Ans : 30 min)
18. E° of In^{3+} , In^+ and Cu^{2+} , Cu^+ are -0.4 V and -0.42 V respectively. Calculate the equilibrium constant for the reaction $\text{In}^{2+} + \text{Cu}^{2+} \longrightarrow \text{In}^{3+} + \text{Cu}^+$ at 25°C .
(Ans : 10^{10})
19. $\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \longrightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}$. Calculate the reduction potential of the half reaction in neutral solution, if all other species to be at unit concentration and the standard reduction potential is 0.78 V .
(Ans : 0.046 V)
20. Discuss the construction and working of lead storage battery.
21. Distinguish between corrosion and passivity.
22. Mention the reasons for corrosion and discuss the preventive methods for corrosion.
23. One normal salt solution surrounding two platinum electrodes, 2.1 cm apart and 6.3 cm^2 in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.
(Ans : $6.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$)
24. Find the number of coulombs needed to plate $10\text{cm} \times 10\text{cm}$ area to a 0.1 mm thickness of copper metal (density 8.94 g cm^{-3}) using aqueous cupric sulphate (At.wt. of Cu is 63.5).
(Ans : 27130 coul)
25. Degree of dissociation of decinormal acetic acid is 3.66% at 25°C . If the equivalent conductance at infinite dilution of acetic acid at 25°C is $390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$, calculate the equivalent conductance at given concentration.
(Ans : $14.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$)
26. When a current strength of 965 amp can deposit 0.9g of Al metal in 20 sec, what is the efficiency of electrolysis?
(Ans : 50%)
27. Certain quantity of electricity is passed through aqueous AgNO_3 and aqueous HCl connected in a series. If 10.8g Silver was deposited, what is the volume of hydrogen collected at one atm and 25°C ?
(Ans : 1.22 L)
28. Potential of normal calomel electrode is -0.28 V . The emf of cell obtained by combining Zn and Cu electrodes of a Daniel cell with normal calomel electrodes are 1.083 V and -0.018 V at 25°C . Determine the EMF of Daniel cell.
(Ans : 1.101 V)
29. The standard potential of Ni^{2+} , Ni is -0.236 V . If this electrode is coupled with a hydrogen electrode, the EMF of the cell becomes zero. Calculate the pH of acid used in electrode.
(Ans : 4)
30. The oxidation power of halogens and the reducing power of halides is just reverse. Support based on the activity series.
(Ans : SRP increases from I_2 to F_2)

31. E^0 for the reaction, $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$, is 0.8 V. Calculate E^0 for the reaction, $\text{Ag}(\text{NH}_3)_2^+ + \text{e}^- \rightarrow \text{Ag} + 2\text{NH}_3$, if the dissociation constant for $\text{Ag}(\text{NH}_3)_2^+$ into NH_3 and Ag^+ is 6×10^{-14} . (Ans : 0.02 V)
32. Standard oxidation potential of iron electrode is + 0.44V. Calculate the potential of Fe, $\text{FeSO}_4(0.1\text{M})$ at 25°C . (Ans : 0.4695V)
33. Colour of potassium iodide solution containing starch turns blue when chlorine water is added. Explain. (Ans : I_2 starch complex is blue)
34. E^0 values of Zn^{2+} , Zn ; Mg^{2+} , Mg and Cu^{2+} , Cu are -0.76V, -2.36 and 0.34V respectively.
 (a) Which metal can be extracted even from its aqueous solutions by electrolysis ?
 (b) Which metal acts as best reductant ? Write reasons. (Hint : (a) Copper; (b) Magnesium)
35. At 298K, the equilibrium constant for the redox reaction $\text{CuSO}_4 + \text{Fe} \rightleftharpoons \text{Cu} + \text{FeSO}_4$ is 2.18×10^{26} . If E^0 of copper is 0.338V, calculate E^0 of iron. (Ans : -0.44V)
36. $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$; $E^0 = + 0.8\text{V}$ and $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$; $E^0 = -0.76\text{V}$. Calculate the cell potential for the reaction, $2\text{Ag} + \text{Zn}^{2+} \rightarrow \text{Zn} + 2\text{Ag}^+$. (Ans : -1.56V)
37. E^0 Values for $\text{Fe}^{3+} 3\text{e}^- \rightarrow \text{Fe}$ and $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$ are -0.036 V and -0.44 V respectively. Calculate E^0 and ΔG^0 for the cell reaction $\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$. (Ans : 0.404 V; -2.4 F)
38. The EMF of the cell, Pt, H_2 (2 atm) | HCl (1M) | H_2 (10atm), Pt is xV and of Pt, Cl_2 (2 atm) | HCl (1M) | Cl_2 (10atm), Pt is yV. How are x and y related ? (Ans : $x = -y$)
39. At 25°C , the EMF of the cell $\text{Zn}, \text{ZnSO}_4 // \text{CuSO}_4, \text{Cu}$ is 0.03V. The temperature coefficient of EMF is $-1.4 \times 10^{-4}\text{V K}^{-1}$. Calculate the enthalpy change of the cell reaction. (Ans : -13.84 kJmol $^{-1}$)
40. The molar conductivity of 0.025 mol L $^{-1}$ methanoic acid is 46.1 S cm 2 mol $^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(\text{H}^+) = 349.6$ S cm 2 mol $^{-1}$ and $\lambda^0(\text{HCOO}^-) = 54.6$ S cm 2 mol $^{-1}$. (Ans : 3.7×10^{-4} mol L $^{-1}$)
41. E_{cell} for the reaction Pt, H_2 (1 atm) / H^+ (1M) // $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ (1/32 M) / H_2 (1 atm), Pt at 300 K is -0.188 V. Calculate the proton concentration and hydrolysis constant of aniline hydrochloride. (Ans : 6.5×10^{-4} M ; 1.35×10^{-5})
42. At 25°C potential of the cell, Pt, H_2 (g), HCl (aq) // AgCl (s), Ag (s) is 0.22 V. If E^0 of silver electrode is 0.8 V, calculate the solubility of AgCl in water. (Ans : 1.2×10^{-5} M)
43. When salt is spread on a road during winter, corrosion of motor cars is a major problem. Justify.
44. $E^0 = - 0.8275\text{V}$ for the reaction, $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$. Calculate the ionic product for the reaction, $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$. (Ans : $9.45 \times 10^{-15}\text{mol}^2\text{L}^{-2}$)
45. E^0 of silver electrode is 0.8 V and solubility product of AgI is 1×10^{-16} . Calculate the potential of silver electrode at 25°C in a saturated AgI solution in water. (Ans : 0.328 V)
46. The cell in which the following reaction occurs : $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$ has $E_{\text{cell}}^0 = 0.236$ V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction. (Ans : -45.5 kJ mol $^{-1}$ and 9.6×10^7)

