Electrochemistry

basic concepts

1. **Electrochemistry:** Electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

2. **Ohm's Law:** It states that the potential difference (V) across the conductor is directly proportional to the current (I) flowing through it. Mathematically,

$$V \propto I \text{ or } V = IR$$

where R is a constant called resistance of the conductor. Ohm's law is obeyed by both the metallic, as well as electrolytic conductors.

3. **Resistance (R):** It is the property of a substance by which it obstructs the flow of electric current through it. The electrical resistance (R) of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A).

Thus, $$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \frac{l}{A}$$

where ρ (rho) is a constant of proportionality called specific resistance or resistivity.

$$\rho = R \frac{A}{l}$$

If $l = 1$ cm and $A = 1$ cm^2 then $R = \rho$.

Thus, resistivity may be defined as the resistance offered by a conductor of 1 cm length with area of cross-section equal to 1 cm^2, *i.e.*, it is the resistance of 1 cm^3 of the conductor.

Units: $\rho = R \frac{A}{l} = \text{ohm} \frac{\text{cm}^2}{\text{cm}} = \text{ohm cm}$

Its SI unit is ohm metre (Ω m).

4. **Conductance (G):** It is the reciprocal of resistance and may be defined as the ease with which the electric current flows through a conductor.

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

Its SI unit is Siemen (S).

$$1 \text{ S} = \text{ohm}^{-1} \text{ (mho)}$$

5. **Conductivity (κ):** It is the reciprocal of resistivity (ρ).

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = G \times \frac{l}{A}$$

If $l = 1$ cm and $A = 1$ cm^2, then $\kappa = G$.

Hence, conductivity of an electrolytic solution may be defined as the conductance of a solution of 1 cm length with area of cross-section equal to 1 cm^2.

Alternatively, it may be defined as the conductance of 1 cm^3 of the solution of an electrolyte.

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Units: $\kappa = \dfrac{1}{\rho} = \dfrac{1}{\text{ohm cm}} = \text{ohm}^{-1}\,\text{cm}^{-1}\,(\text{S cm}^{-1})$

The SI unit of conductivity is S m^{-1}.

6. **Factors Affecting Metallic Conductance**

   Electrical conductance through metal is called metallic or electronic conductance and is due to the movement of electrons. It depends on:

   (*a*) The nature and structure of metal.

   (*b*) The number of valence electrons per atom.

   (*c*) Temperature (it decreases with increase in temperature).

7. **Factors Affecting Electrolytic Conductance**

   Electrolyte: An electrolyte is a substance that dissociates in solution to produce ions and hence conduct electricity in dissolved or molten state.

   Examples: HCl, NaOH, KCl (Strong electrolytes).

   CH_3COOH, NH_4OH (Weak electrolytes).

   The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. The following factors govern the flow of electricity through a solution of electrolyte.

   (*a*) **Nature of electrolyte or interionic attractions:** Lesser the solute–solute interactions, greater will be the freedom of movement of ions and higher will be the conductance.

   (*b*) **Solvation of Ions:** Larger the magnitude of solute–solvent interactions, greater is the extent of solvation and lower will be the electrical conductance.

   (*c*) **The nature of solvent and its viscosity:** Larger the solvent–solvent interactions, larger will be the viscosity and more will be the resistance offered by the solvent to flow of ions and hence lesser will be the electrical conductance.

   (*d*) **Temperature:** As the temperature of electrolytic solution rises solute–solute, solute–solvent and solvent–solvent interactions decrease, which results in the increase of electrolytic conductance.

8. **Difference between Metallic and Electrolytic Conductance**

S.No.	Metallic Conductance	Electrolytic Conductance
(*i*)	Movement of electrons is responsible for conduction.	Movement of ions is responsible for conduction.
(*ii*)	Does not involve transfer of matter.	Matter moves in the form of ions.
(*iii*)	Decreases with increase in temperature as kernels start vibrating which produce hindrance in the flow of electrons.	Increases with increase in temperature due to decrease in interionic attraction or increase in dissociation.

9. **Measurement of Conductance:** As we know, $\kappa = \dfrac{1}{R} \times \dfrac{l}{A}$

   The value of κ could be known, if we measure l, A and R. The value of the resistance of the solution between two parallel electrodes is determined by using 'Wheatstone' bridge method (Fig. 3.1).

   It consists of two fixed resistance R_3 and R_4, a variable resistance R_1 and the conductivity cell having the unknown resistance R_2. The bridge is balanced when no current passes through the detector. Under these conditions,

   $$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{or} \quad R_2 = \frac{R_1 R_4}{R_3}$$

Fig. 3.1: Wheatstone Bridge

   Knowing the values of R_1, R_3 and R_4 the resistance of the solution, R_2 is determined. The reciprocal of R_2 gives the conductance of the solution.
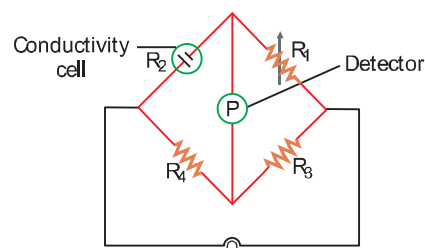
10. **Molar Conductivity (Λ_m):** It may be defined as the conducting power of all the ions produced by dissolving one gram mole of an electrolyte placed between two large electrodes at one centimetre apart. Mathematically,

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{c}$$

where, V is the volume of solution in cm^3 containing 1 gram mole of electrolyte and c is the molar concentration.

Units: $\Lambda_m = \dfrac{\kappa \times 1000}{c} = \dfrac{S\ cm^{-1}}{mol\ cm^{-3}}$

$$= ohm^{-1}\ cm^2\ mol^{-1}\ or\ S\ cm^2\ mol^{-1}$$

11. **Variation of Conductivity and Molar Conductivity with Concentration:**

Conductivity decreases with the decrease in concentration, this is because the number of ions per unit volume that carry the current in the solution decreases on dilution.

Molar conductivity ($\Lambda_m = \kappa \times V$) increases with the decrease in concentration or increase in dilution. This is because the total volume V of solution containing one mole of electrolyte increases with increase in dilution. It has been found that the decrease in κ on dilution of a solution is more than compensated by increase in its volume.

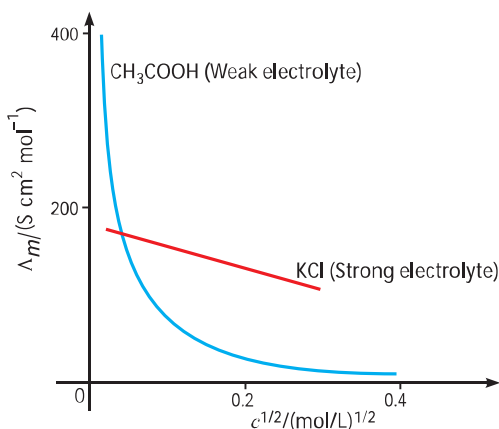**Graphical representation of the variation of Λ_m vs $\sqrt{c}$**

Fig. 3.2: Λ_m vs $\sqrt{c}$ for weak and strong electrolytes

Limiting Molar Conductivity (Λ^o_m): The limiting value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution.

It is possible to determine the molar conductivity at infinite dilution (Λ^o_m) in case of strong electrolyte by extrapolation of curve of Λ_m vs $\sqrt{c}$ (Fig. 3.2). On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve as the curve becomes almost parallel to y-axis when concentration approaches to zero.

The mathematical relationship between Λ_m and Λ^o_m for strong electrolyte was developed by Debye, Huckel and Onsager. In simplified form, the equation can be given as

$$\Lambda_m = \Lambda^o_m - bc^{1/2}$$

where Λ^o_m is the molar conductivity at infinite dilution and b is a constant which depends on the nature of the solvent and temperature.

12. **Kohlrausch's Law:** It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

In general, if an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by

$$\Lambda_m^o = v_+ \lambda_+^o + v_- \lambda_-^o$$

Here, λ_+^o and λ_-^o are the limiting molar conductivities of cations and anions, respectively.

Applications of Kohlrausch's Law:

(a) **Calculation of molar conductivities of weak electrolyte at infinite dilution:** For example, molar conductivity of acetic acid (weak acid) at infinite dilution can be obtained from the knowledge of molar conductivities at infinite dilution of strong electrolytes like HCl, CH_3COONa and NaCl as illustrated below:

$$\Lambda_{m(CH_3COOH)}^o = \lambda_{CH_3COO^-}^o + \lambda_{H^+}^o$$

$$= [\lambda_{CH_3COO^-}^o + \lambda_{Na^+}^o] + [\lambda_{H^-}^o + \lambda_{Cl^-}^o] - [\lambda_{Na^+}^o + \lambda_{Cl^-}^o]$$

i.e., $\quad \Lambda_{m(CH_3COOH)}^o = \Lambda_{m(CH_3COONa)}^o + \Lambda_{m(HCl)}^o - \Lambda_{m(NaCl)}^o$

(b) **Determination of degree of dissociation of weak electrolytes:**

Degree of dissociation $(\alpha) = \dfrac{\Lambda_m^c}{\Lambda_m^o}$

(c) **Determination of dissociation constant (K) of weak electrolytes:**

$$K = \dfrac{c\alpha^2}{1-\alpha}$$

Also, $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^o}$

$\therefore \quad K = \dfrac{c(\Lambda_m^c/\Lambda_m^o)^2}{1 - \Lambda_m^c/\Lambda_m^o} = \dfrac{c(\Lambda_m^c)^2}{\Lambda_m^o(\Lambda_m^o - \Lambda_m^c)}$

(d) **Determination of solubility of sparingly soluble salts:**

$$\Lambda_m^o = \dfrac{\kappa \times 1000}{Molarity} = \dfrac{\kappa \times 1000}{Solubility} \quad \text{or, Solubility} = \dfrac{\kappa \times 1000}{\Lambda_m^o}$$

13. **Electrochemical Cells:** An electrochemical cell is a device in which chemical energy of the redox reaction is converted into electrical energy. The redox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy.

The simplest electrochemical cell is Daniel cell or Galvanic cell in which a zinc rod is placed in a solution of Zn^{2+} ions (say, $ZnSO_4$) in the left container and a bar of copper metal is immersed in a solution of Cu^{2+} ions (say, $CuSO_4$) in the right container. The two metals which act as electrodes are connected by a metallic wire through a voltmeter. The two solutions are joined by an inverted U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly. This arrangement of U-tube is called salt bridge (Fig. 3.3).
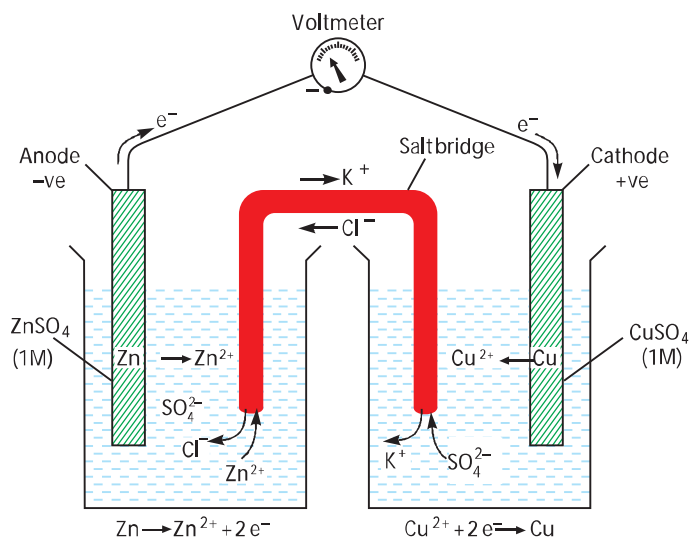

Fig. 3.3: A simple voltaic cell

The overall cell reaction,

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

can be split into two half cells. The deflection in the voltmeter indicates the flow of current through the external circuit. The conventional current flows through the outer circuit from copper metal to zinc metal, which implies flow of electrons from zinc to copper bar.

(a) At zinc electrode, the metal undergoes oxidation and releases two electrons.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \text{ (oxidation)}$$
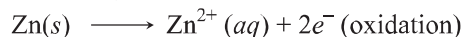
Because oxidation is taking place, the electrode behaves as anode. These electrons travel through wire and reach the copper metal.

(b) $$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \text{ (reduction)}$$

The above reaction occurs at the copper electrode. Electronation takes place which is a reduction process and that is why it acts as cathode.

As a result of the two half cell reactions, zinc metal dissolves in anode solution to form Zn^{2+} ions, while the Cu^{2+} ions are discharged at the cathode by accepting two electrons and are deposited at cathode. The electrical neutrality is maintained in two half cells using a salt bridge. The anions of the inert electrolyte in the salt bridge migrate to the anodic chamber and cations to the cathodic chamber.

As a result, as the reaction progresses, copper bar gains weight whereas zinc rod loses weight. As a consequence, the cell continues to function till either zinc metal or copper ions in solution are consumed fully.

Since electrons are released at anode, it acquires negative polarity and cathode becomes positive because it needs electrons for the reduction of +ve ions. This observation is against the usual electrolytic cell where anode is +ve and cathode is −ve.

Salt Bridge and Its Functions

A commonly used form of salt bridge consists of a glass U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly.

The electrolytes that are often used in salt bridge are called inert electrolytes which are supposed:

(a) not to interact chemically with either of the solutions present in anodic or cathodic chamber.

(b) not to interfere with overall cell reaction.

(c) only those electrolytes can be used in a salt bridge in which mobility of ions is almost the same. Example, KCl, K_2SO_4, etc.

A salt bridge carries out two important functions:

(a) It allows only flow of ions through it. Thus, the circuit is completed.

(b) It also maintains the electrical neutrality.

14. **Cell Diagram or Representation of an Electrochemical Cell:** The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations: The Daniel cell is represented as follows:

$$Zn(s) \,|\, Zn^{2+}(c_1) \,||\, Cu^{2+}(c_2) \,|\, Cu(s)$$

(a) Anode half cell is written on the left hand side while cathode half cell on right hand side.

(b) A single vertical line separates the metal from aqueous solution of its own ions.

$$Zn(s) \,|\, Zn^{2+}(aq); \qquad Cu^{2+}(aq) \,|\, Cu(s)$$
$$\text{Anodic chamber} \qquad \text{Cathodic chamber}$$

(c) A double vertical line represents salt bridge which allows the passage of ions through it but prevents the mixing of two solutions.

(d) The molar concentration (c) is placed in brackets after the formula of the corresponding ion.

(e) The value of EMF of the cell is written on the extreme right of the cell. For example,

$$Zn(s) \,|\, Zn^{2+}(1M) \,||\, Cu^{2+}(1M) \,|\, Cu(s) \qquad\qquad EMF = +1.1 \text{ V}$$
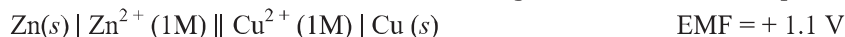
(f) If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket, say for example, when a zinc anode is connected to a hydrogen electrode.

$$Zn(s) \,|\, Zn^{2+}(c_1) \,||\, H^+(c_2) \,|\, H_2 \,(Pt)$$

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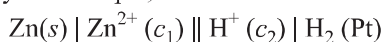
15. Reversibility of Daniel Cell:

(a) When external voltage is less than 1.10 V, electrons flow from Zn to Cu but current flows from Cu to Zn, *i.e.*, in opposite direction. Zinc dissolves at anode and copper deposits at cathode [see Fig. 3.4(*a*)]

(b) When external voltage applied is less than 1.10 V and is increased slowly, it is observed that the reaction continues to take place till the external voltage attains the value 1.10 V. When this is so, reaction stops altogether and no current flows [see Fig. 3.4(*b*)].

(c) If the value of external voltage exceeds the voltage of Daniel cell (1.10 V), the reaction takes place in opposite direction, *i.e.*, the cell functions like an electrolytic cell [see Fig. 3.4(*c*)].
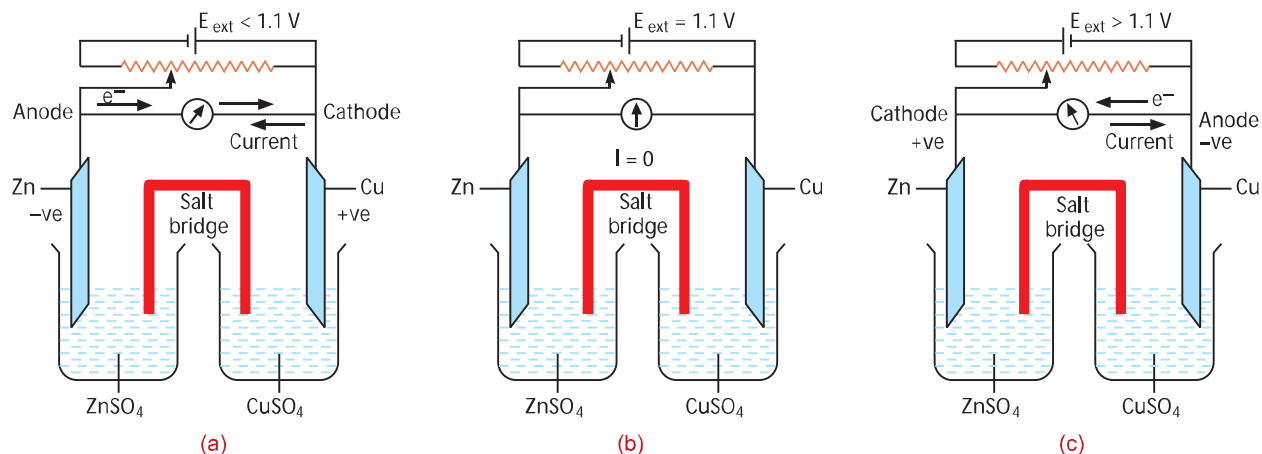
Fig. 3.4: Functioning of Daniel cell when external voltage E_{ext} opposing the cell potential is applied

16. Electrode Potential:
It may be defined as the tendency of a metal, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged.

The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.

$$M(s) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^-$$

Or

$$M^{n+}(aq) + ne^- \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} M(s)$$
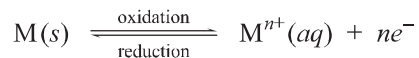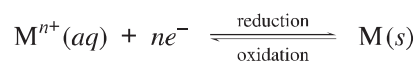
Characteristics:

(a) Both oxidation and reduction potentials are equal in magnitude but opposite in sign.

(b) The reduction potential shows an increase with increasing concentration and decrease with decreasing concentration of ions in a solution.

(c) It is not a thermodynamic property, so values of E are not additive.
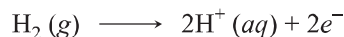
17. Standard Hydrogen Electrode (SHE):
It is a reference electrode and its reduction potential is arbitrarily assigned as zero volt at all temperature.

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution having 1M concentration of H^+ ions. Pure hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a temperature of 298 K (Fig. 3.5).

The hydrogen electrode can act both ways—as an anode or as a cathode.

Acting as anode — oxidation takes place,

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

Acting as cathode — reduction takes place,

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$
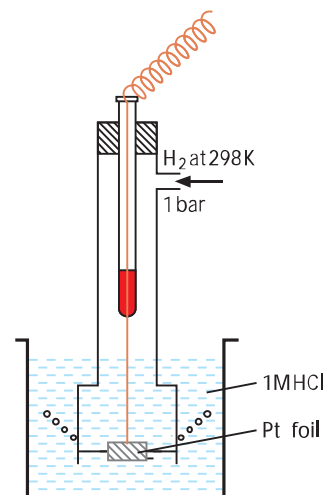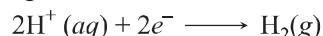
Fig. 3.5: Standard or Normal Hydrogen Electrode

Representation of SHE

$$Pt(s) \,|\, H_2 \,(g) \,|\, H^+ \,(aq) \,(c = 1\ M)$$

18. **Standard Electrode Potential (E^0):** It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are:

    (*a*) 1 M concentration of each ion in the solution.

    (*b*) A temperature of 298 K.

    (*c*) 1 bar pressure for each gas.

19. **Cell Potential or EMF of a Cell:** The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

    $$E_{cell} = E_{reduction} - E_{oxidation} = E_{cathode} - E_{anode}$$

    Since anode is put on left and cathode on right, therefore it follows

    $$E_{cell} = E_R - E_L$$

    For a Daniel cell,

    $$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn}$$
    $$= 0.34V - (-0.76V)$$
    $$= 1.10V$$

20. **Nernst Equation:** It relates electrode potential with the concentration of ions.

    For an electrode reaction, $M^{n+}\,(aq) + ne^- \longrightarrow M(s)$

    Nernst equation can be written as

    $$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

    $$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

    where, $E_{M^{n+}/M}$ = Electrode potential

    $E^o_{M^{n+}/M}$ = Standard electrode potential

    $R = 8.314\ JK^{-1}\ mol^{-1}$

    T = Temperature in kelvin

    n = No. of electrons gained
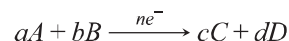
    F = Faraday constant (96500 C mol^{-1})

    Substituting the value of R and F, we get

    $$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}, \text{ at 298 K}$$

    or $\qquad E_{M^{n+}/M} = E^o_{M^{n+}/M} + \frac{0.0591}{n} \log [M^{n+}], \text{ at 298 K}$

    Thus, the reduction potential increases with the increase in the concentration of ions.

    For a general electrochemical reaction of the type:

    $$aA + bB \xrightarrow{ne^-} cC + dD$$

    Nernst equation can be given as

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

    $$E_{cell} = E^o_{cell} - \frac{2.303}{nF} RT \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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Substituting the values of R and F we get

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ at 298 K}$$

21. **Equilibrium Constant from Nernst Equation:** For a Daniel cell, at equilibrium

$$E_{cell} = 0 = E^o_{cell} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or

$$E^o_{cell} = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium, $\dfrac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$

$\therefore$

$$E^o_{cell} = \frac{2.303RT}{2F} \log K_c$$

$$E^o_{cell} = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log K_c = \frac{0.0591}{2} \log K_c$$

In general, $E^o_{cell} = \dfrac{0.0591}{n} \log K_c$ or, $\log K_c = \dfrac{n}{0.0591} E^o_{cell}$

22. **EMF and Gibbs Free Energy:** The work done by a reversible galvanic cell is equal to decrease in its free energy.

Mathematically, $\Delta_r G = -nFE_{cell}$

If concentration of all the reacting species is unity, then,
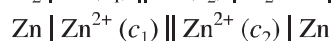
$$E_{cell} = E^o_{cell} \text{ and we get}, \Delta_r G^o = -nFE^o_{cell}$$

From $\Delta_r G^o$, we can calculate the equilibrium constant of a reaction,

$$\Delta_r G^o = -RT \ln K_c \text{ or } \Delta_r G^o = -2.303\, RT \log K_c$$

23. **Electrochemical Series:** The arrangement of various standard half-cells in the order of their decreasing standard reduction potential values is known as electrochemical series.

   ● A negative value of E^o means that the redox couple is stronger reducing agent than H^+/H_2. *e.g.*, Mg (-2.36).
   ● A positive value of E^o means that the redox couple is weaker reducing agent than H^+/H_2. *e.g.*, Br_2 (1.09).

24. **Concentration Cells:** If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells. In these cells, oxidation takes place on the electrode with lower concentration (c_1) while reduction takes place on the electrode with higher concentration (c_2). For example,

   $H_2 \,|\, H^+(c_1) \,\|\, H^+(c_2) \,|\, H_2$; $Cu \,|\, Cu^{2+}(c_1) \,\|\, Cu^{2+}(c_2) \,|\, Cu$
   $Zn \,|\, Zn^{2+}(c_1) \,\|\, Zn^{2+}(c_2) \,|\, Zn$

The EMF of concentration cell at 298 K is given by

$$E_{cell} = \frac{0.0591}{n} \log \frac{c_2}{c_1}, \text{ where } c_2 > c_1$$

25. **Electrolysis:** The process of decomposition of an electrolyte when electric current is passed through its aqueous solution or fused state is called electrolysis.

The process of electrolysis of a substance is governed by Faraday's laws of electrolysis.

(*a*) Faraday's first law of electrolysis

"The amount of any substance deposited or liberated at the electrode is directly proportional to the quantity of electricity passing through the electrolyte."

If w grams of the substance deposited on passing Q coulombs of electricity, then

$$w \propto Q \quad \text{or} \quad w \propto I \times t \qquad\qquad [\because Q = I \times t]$$

or
$$w = Z \times I \times t$$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

- **Electrochemical equivalent (Z):** If $I = 1$ ampere and $t = 1$ second, then

$$w = Z$$

Thus, the electrochemical equivalence may be defined as the amount of the substance deposited by passing one ampere of current for one second or by passing one coulomb of charge through the electrolyte.

- 1 Faraday = Quantity of electricity carried by 1 mole of electrons.
  $(6.023 \times 10^{23} \text{ mol}^{-1} \times 1.6 \times 10^{-19} \text{ C} = 96472 \text{ C mol}^{-1} \simeq 96500 \text{ C mol}^{-1})$

- If n mol of electrons are involved in an electrode reaction, then

  $n \times 96500$ C of charge will deposit $= M$ g of the element

  1 C of charge will deposit $= \dfrac{M}{n \times 96500}$ g of element

  But 1 C of charge deposit mass of element $= Z$ g

  $\therefore$ $\qquad\qquad Z = \dfrac{M}{n \times 96500} \text{g} = \dfrac{E}{96500} \text{g}$

  where E is the equivalent mass of the element and is equal to $\dfrac{\text{Atomic mass}}{\text{Valency}}$ of the element.

  or $\qquad\qquad E = 96500 \times Z$

- **Equivalent mass:** The mass of an element deposited by passing 96500 C of charge.

(b) **Faraday's second law of electrolysis**

"When same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent masses."
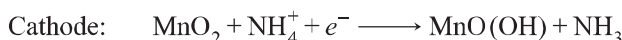
Mathematically, $\qquad\qquad \dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$

26. **Commercial Cells (Batteries):** Batteries are the electrochemical cells used commercially to generate electricity. "Any battery consists of two or more than two galvanic cells connected in series where the chemical energy of the redox reactions is converted into electrical energy." There are mainly two types of batteries:

(a) **Primary cells (Batteries):** These cells are not chargeable because the electrode reaction occurs only once and after the use over a period of time the cells become dead and cannot be reused.

The most familiar example of this type of cell is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in watches, radios, calculators, etc. It consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and $ZnCl_2$ (Fig. 3.6).

Carbon rod (cathode)

Zinc cup (anode)

MnO_2 + Carbon black + NH_4Cl paste

Fig. 3.6: The dry cell

The electrode reactions are:

Anode: $\qquad\qquad Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $\quad MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$
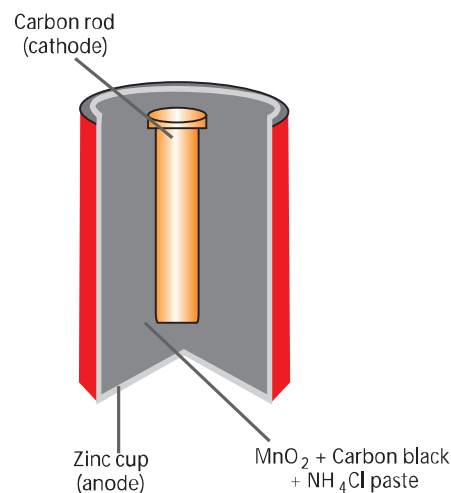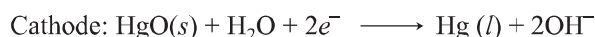
The cell has a potential of nearly 1.5 V.

Electrochemistry

Another type of primary cell is the mercury cell, consisting of zinc–mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:

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

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

The cell potential is approximately 1.35 V and remains constant as the ionic concentration of the solution is not changed during its life.

(b) Secondary cells (Batteries)

A secondary battery is rechargeable and can be used again and again. It is recharged by passing current through it from an external source. Most familiar example of secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode.

A 38% solution of H_2SO_4 is used as an electrolyte (Fig. 3.7).

Fig. 3.7: The lead storage battery

The cell reactions when the battery is in use, are:

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

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

The overall reaction is:

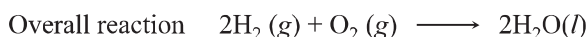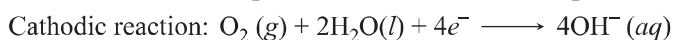$\quad Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$
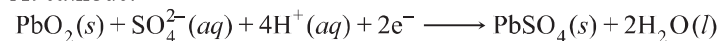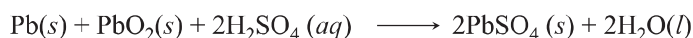
On recharging the cell, operated like an electrolytic cell; the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

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

At cathode: $\quad PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$
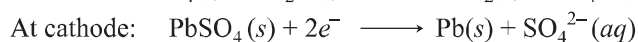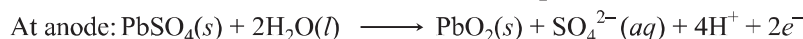
Another important secondary cell is the nickel–cadmium cell which has longer life than the lead storage cell but is costly. Here, the overall reaction during discharge of the battery is

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

27. **Fuel Cells:** Fuel cells are those cells which produce electrical energy directly from the combustion of fuels such as hydrogen, carbon monoxide or methane. The most successful fuel cell, H_2–O_2 cell utilises the reaction between hydrogen and oxygen to produce water. Hydrogen and oxygen are bubbled through a porous carbon electrode in the cell into concentrated aqueous sodium hydroxide. Catalysts are incorporated into the electrode (Fig. 3.8). The electrode reactions are

Fig. 3.8: A simple H_2–O_2 fuel cell

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

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

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

Advantages of Fuel Cells:

(a) It is a pollution-free device since no harmful products are formed.

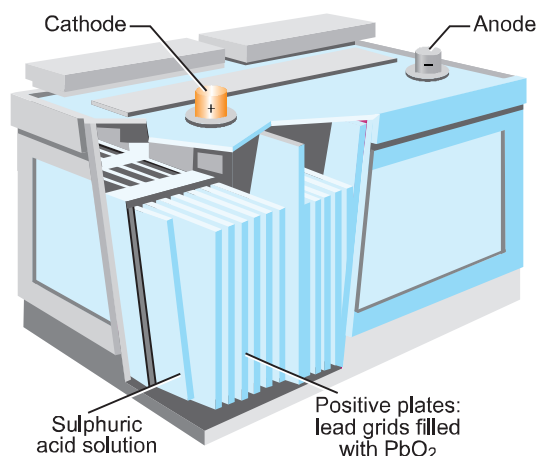(b) Its efficiency is about 75% which is considerably higher than conventional cells.
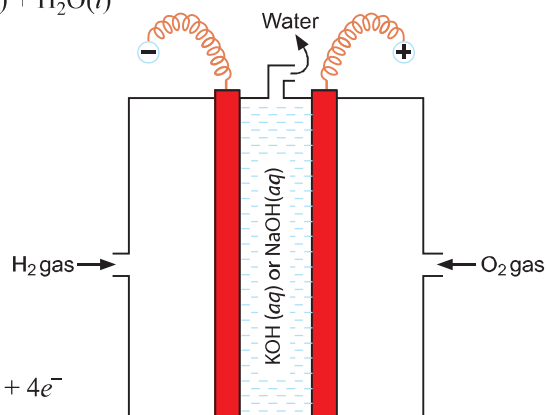
(*c*) These cells are light in weight as compared to electrical generators to produce corresponding quantity of power.

(*d*) It is a continuous source of energy if the supply of gases is maintained.

28. **Corrosion:** The process of slow eating up of metals by gases and water vapours present in atmosphere due to the formation of certain compounds like oxides, sulphides, carbonates, etc. is called corrosion. Corrosion of iron is known as rusting. Chemically, rust is hydrated ferric oxide, $Fe_2O_3.xH_2O$. Corrosion may be considered as an electrochemical phenomenon. According to electrochemical theory of rusting, the impure iron surface behaves like a small electrochemical cell in the presence of moisture containing oxygen or carbon dioxide. Such a cell is called corrosion cell or corrosion couple. In these miniature corrosion cells, pure iron acts as anode, impure surface area acts as cathode and moisture having dissolved carbon dioxide or oxygen acts as electrolyte.

At anode, oxidation of iron takes place. Thus, Fe enters into the solution as Fe^{2+} ions leaving behind electrons which are pushed into cathodic area.

$$Fe \longrightarrow Fe^{2+} + 2e^-; \quad E^o_{Fe^{2+}/Fe} = -0.44 \text{ V} \qquad \qquad ...(i)$$

At cathode, the electrons are picked up by the H^+ ions which are produced from H_2CO_3 (formed due to dissolution of CO_2 in moisture) or from H_2O.
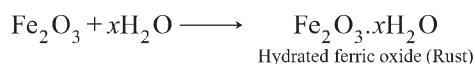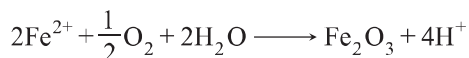
$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$
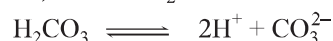
H^+ ions, thus formed, reduces the dissolved oxygen as the net reaction at the cathodic area is

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O; \quad E^o_{H^+/O_2/H_2O} = 1.23 \text{ V} \qquad \qquad ...(ii)$$
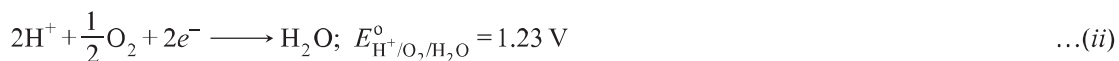
The overall reaction of the corrosion cell can be obtained by adding equations (*i*) and (*ii*)

$$Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O; \quad E^o_{cell} = 1.67 \text{ V}$$
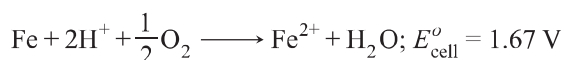
The ferrous ions so formed move through water and come at the surface where these are further oxidised by atmospheric oxygen to ferric ions and form rust which is hydrated ferric oxide (Fig. 3.9).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3.xH_2O}$$

29. **Prevention of Corrosion:** The metal surface can be protected against corrosion by the following methods:

(*a*) **Barrier protection:** A thin film is introduced between iron and atmospheric oxygen, carbon dioxide and moisture. The following methods are adopted for depositing thin film on metal surface:

Fig. 3.9: Corrosion

(*i*) By covering the surface with paint or a thin film of grease.

(*ii*) By electroplating iron with some non-corrosive metals such as nickel, chromium, copper, etc.

(*b*) **Sacrificial protection:** In this method, iron surface is covered with a more electropositive metal than iron which gets oxidised in preference to iron. In such a situation the more electropositive metal loses electrons instead of iron and thus this metal is sacrificed at the cost of iron, hence the name sacrificial protection. Iron is generally coated with zinc and this process is called galvanization.

(*c*) **Electrical protection:** This is also a case of sacrificial protection. This method is used for the protection of underground water pipes or iron tanks. In this method, the exposed surface of iron is protected by connecting it to a block of some active metal such as magnesium, aluminium or zinc (Fig. 3.10). This more electropositive metal acts as anode and lose electrons in preference to iron. The iron surface acts as cathode. This method, therefore, is also called cathodic protection. The electrons released at the anode are accepted by H^+ ions of water at the surface of iron. More electropositive metal is consumed gradually in the process and needs periodical replacement.
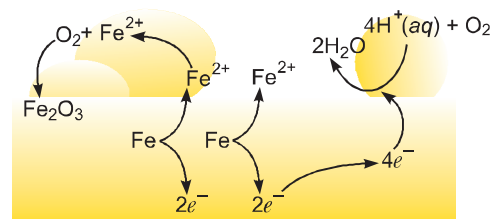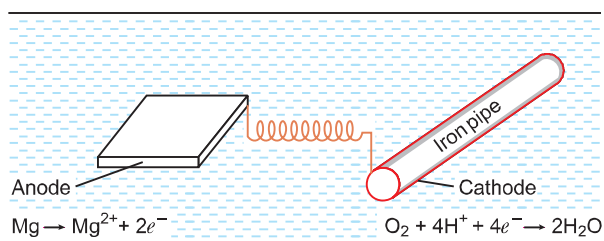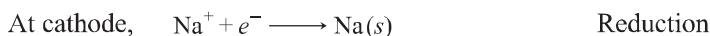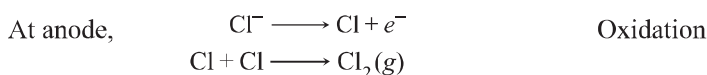
Electrochemistry

30. **Products of Electrolysis:** Under the influence of electric current through molten electrolytes or their aqueous solutions, ions move towards oppositely charged electrodes. Many times the electrode products differ. For example, the electrolysis of molten sodium chloride yields sodium metal at the cathode and chlorine gas is liberated at the anode.
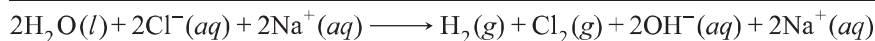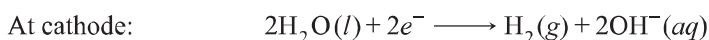
$$NaCl(s) \underset{\text{(molten state)}}{\longrightarrow} Na^+ + Cl^-$$

At anode,
$$Cl^- \longrightarrow Cl + e^- \qquad\qquad \text{Oxidation}$$
$$Cl + Cl \longrightarrow Cl_2(g)$$

At cathode, $\quad Na^+ + e^- \longrightarrow Na(s) \qquad\qquad$ Reduction

However, when a concentrated aqueous solution of sodium chloride is electrolysed, H_2 gas at cathode and Cl_2 gas at anode are obtained. This is because water is preferably reduced at cathode.

At cathode, $\qquad 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
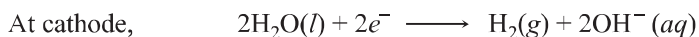
This happens because the standard reduction potential of water is greater than the standard reduction potential of Na^+ ion.

$$Na^+(aq) + e^- \longrightarrow Na(s) \qquad\qquad E^o_{cell} = -2.71 \text{ V}$$
$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad\qquad E^o_{cell} = -0.83 \text{ V}$$
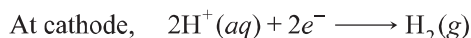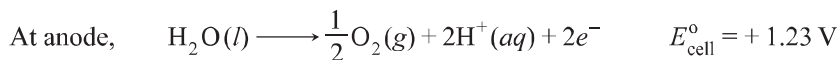
At anode, however, Cl_2 gas is liberated because of over potential of oxygen. In fact, the remaining solution after electrolysis yields solid NaOH on evaporating. Thus,

At anode $\qquad\qquad 2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$

At cathode: $\qquad\qquad 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

$$\overline{2H_2O(l) + 2Cl^-(aq) + 2Na^+(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq) + 2Na^+(aq)}$$

(*a*) **Electrolysis of dilute H_2SO_4**

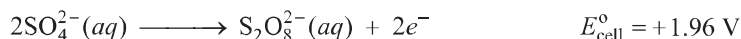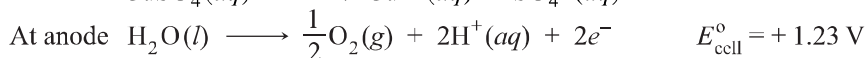During electrolysis of dilute H_2SO_4, the products are $H_2(g)$ at cathode and $O_2(g)$ at anode:

$$H_2SO_4 \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

At anode, $\quad H_2O(l) \longrightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \qquad E^o_{cell} = +1.23 \text{ V}$

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

If H_2SO_4 is concentrated then the following reaction occurs at anode

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^- \quad E^o_{cell} = +1.96 \text{ V}$$
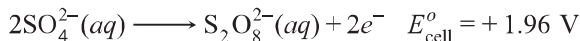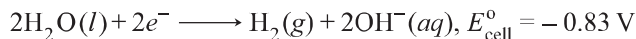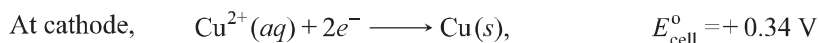
(*b*) **Electrolysis of aqueous copper sulphate using inert electrodes (Pt)**

In this, copper is deposited at cathode and oxygen is liberated at anode.

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

At anode $\quad H_2O(l) \longrightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \qquad E^o_{cell} = +1.23 \text{ V}$

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^- \qquad\qquad E^o_{cell} = +1.96 \text{ V}$$

Water, having low E^o, would be preferably oxidised at anode instead of SO_4^{2-} ions.

Cu^{2+} ions have greater reduction potential, copper metal is deposited at the cathode.

At cathode, $\qquad Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s), \qquad\qquad E_{cell}^o = +0.34\ V$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq),\ E_{cell}^o = -0.83\ V$$

(c) If $CuSO_4$ is electrolysed between two copper electrodes (active electrodes), the Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction occurs

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
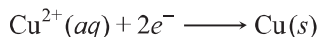
Thus, copper metal is deposited at cathode. At the anode, copper is converted into Cu^{2+} ions with the following change:

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

Thus, copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This forms the basis of an industrial process in which impure copper is converted into copper of high purity. The impure copper is made as anode that dissolves on passing current and pure copper is deposited at cathode.

(d) **Electrolysis of aqueous sodium bromide:** Like aqueous NaCl, the electrode products are Br_2 (l) at anode and H_2 (g) at cathode.

Conclusions: 1. Cathodic reaction will be one which has higher $E_{reduction}^o$ value.

2. Anodic reaction will be one which has higher $E_{oxidation}^o$ value or lower $E_{reduction}^o$ value.

Important Formulae

1. $R = \rho\left(\dfrac{l}{A}\right) = \rho \times$ Cell constant

   where, R = Resistance

   A = Area of cross-section of the electrodes

   ρ = Resistivity

2. $\kappa = \dfrac{1}{R} \times$ cell constant

   where, κ = Conductivity or specific conductance

3. $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

   where, Λ_m = Molar conductivity

   M = Molarity of the solution.

4. $\Lambda_m^o(A_x B_y) = x\Lambda_m^o(A^{y+}) + y\Lambda_m^o(B^{x-})$

   where, Λ_m^o = Molar conductivity at infinite dilution, x and y are the number of cations and anions produced by one formula unit of the electrolyte on complete dissociation.

5. $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^o}$

   where, α = Degree of dissociation

   Λ_m^c = Molar conductivity at a given concentration

6. For a weak binary electrolyte AB
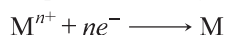
   $K = \dfrac{c\alpha^2}{1-\alpha} = \dfrac{c(\Lambda_m^c)^2}{\Lambda_m^o(\Lambda_m^o - \Lambda_m^c)}$

   where, K = Dissociation constant

Electrochemistry

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$
$$= E^o_{right} - E^o_{left}$$

7. Nernst equations for a general electrode reaction:
$$M^{n+} + ne^- \longrightarrow M$$
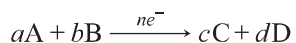$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$
$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303\,RT}{nF} \log \frac{1}{[M^{n+}]}$$
$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \quad \text{at 298 K}$$

8. Nernst equation for a general electrochemical reaction:
$$aA + bB \xrightarrow{\;ne^-\;} cC + dD$$
$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
$$E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{at 298 K}$$

9. $\log K_c = \dfrac{n}{0.0591} E^o_{cell}$

   where, K_c = Equilibrium constant

10. $\Delta_r G^o = -nFE^o_{cell}$

   $\Delta_r G^o = -2.303RT \log K_c$

   where, $\Delta_r G^o$ = Standard Gibbs energy of the reaction

11. $Q = I \times t$

   where Q = Quantity of charge in coulombs

   I = Current in amperes

   t = Time in seconds

12. $m = Z \times I \times t$

   where m = Mass of the substance deposited at the electrodes

   Z = Electrochemical equivalent
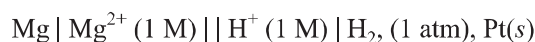
NCERT Textbook Questions

NCERT Intext Questions

Q. 1. **How would you determine the standard electrode potential of the system $Mg^{2+}\,|\,Mg$?**

Ans. Set up an electrochemical cell consisting of $Mg\,|\,MgSO_4$ (1 M) as one electrode by dipping a magnesium rod in 1 M $MgSO_4$ solution and standard hydrogen electrode Pt, H_2 (1 atm) | H^+ (1 M) as the second electrode as shown in given figure.
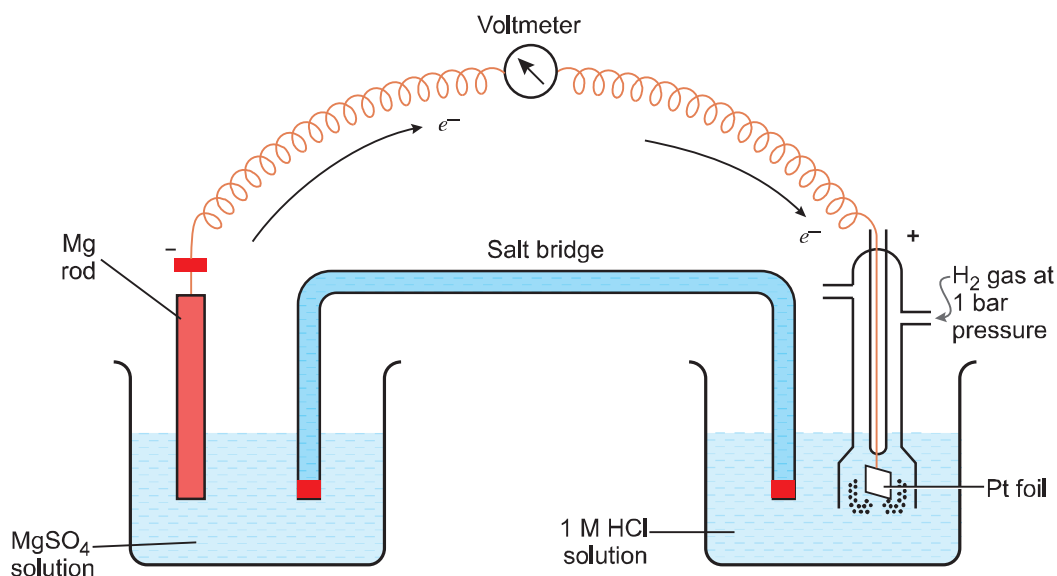
Measure the EMF of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that electrons flow from magnesium electrode to hydrogen electrode. Thus, the cell may be represented as follows:

$$Mg \,|\, Mg^{2+} \,(1\ M) \,||\, H^+ \,(1\ M) \,|\, H_2, \,(1\ atm), \,Pt(s)$$

$$E^o_{cell} = E^o_{H^+/\frac{1}{2}H_2} - E^o_{Mg^{2+}/Mg}$$

But

$$E^o_{H^+/\frac{1}{2}H_2} = 0$$

Hence,

$$E^o_{Mg^{2+}/Mg} = -\,E^o_{cell}$$

Q. 2. Can you store copper sulphate solutions in a zinc pot?   [*HOTS*]

Ans. For this we have to check whether the following reaction will take place or not.

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$
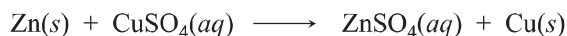
$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn} = 0.34 - (-0.76) = 1.10\ V$$

As E^o_{cell} is positive, the reaction will take place. Therefore, we cannot store copper sulphate in zinc pot.

Q. 3. Consult the table of the standard electrode potential and suggest three substances that can oxidise ferrous ions under suitable conditions.

Ans. Oxidation of ferrous ions means

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-; \ E^o_{Fe^{3+}/Fe^{2-}} = 0.77\ V$$
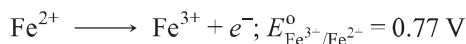
Only those substances can oxidise Fe^{2+} to Fe^{3+} which are stronger oxidising agents and have positive reduction potentials greater than 0.77 V so that E_{cell} of the cell reaction is positive. This is for elements lying below Fe^{3+}/Fe^{2+} in the electrochemical series, for example, Br_2, Cl_2 and F_2.

Q. 4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.   [*HOTS*]

Ans. For hydrogen electrode

$$H^+ + e^- \longrightarrow \tfrac{1}{2} H_2$$
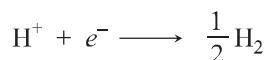
$$E_{H^+/\frac{1}{2}H_2} = E^o_{H^+/\frac{1}{2}H_2} - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$

Here, $n = 1$,

$$\log \frac{1}{[H^+]} = pH = 10, \ E^o_{H^+/\frac{1}{2}H_2} = 0$$

∴

$$E_{H^+/\frac{1}{2}H_2} = 0 - 0.0591 \times 10 = -\,\mathbf{0.591\ V}$$

Electrochemistry

Q. 5. Calculate the emf of the cell in which the following reaction takes place:

$$Ni(s) + 2Ag^+(0.002\ M) \longrightarrow Ni^{2+}(0.160\ M) + 2Ag(s)$$

Given that $E^o_{cell} = 1.05\ V$

Ans. From Nernst equation to the given cell reaction

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05\ V - \frac{0.0591}{2} \log \frac{0.160}{(0.002)^2} = 1.05 - \frac{0.0591}{2} \log(4 \times 10^4)$$

$$= 1.05 - \frac{0.0591}{2}(4.6021) = 1.05 - 0.14\ V = \mathbf{0.91\ V}$$

Q. 6. The cell in which the following reaction occurs:

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$$
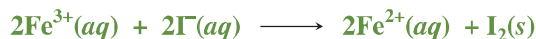
has $E^o_{cell} = 0.236\ V$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans. $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ or $2I^- \longrightarrow I_2 + 2e^-$

Thus, for the given cell reaction, $n = 2$.

$$\Delta_r G^o = -nFE^o_{cell} = -2 \times 96500 \times 0.236\ J\ mol^{-1} = -45548\ J\ mol^{-1} = \mathbf{-45.55\ kJ\ mol^{-1}}$$

$$\Delta_r G^o = -2.303\ RT \log K_c$$

$$-\log K_c = \frac{\Delta_r G^o}{2.303\ RT} = \frac{-45.55\ kJ\ mol^{-1}}{2.303 \times 8.314 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1} \times 298K} = -7.983$$

$$\therefore \quad K_c = \text{Antilog}\ (7.983) = \mathbf{9.616 \times 10^7}$$

Q. 7. Why does the conductivity of a solution decrease with dilution?

Ans. Conductivity of a solution is the conductance of ions present in a unit volume of the solution. On dilution, the number of ions per unit volume decreases. So, the conductivity also decreases.

Q. 8. Suggest a way to determine the Λ^o_m value of water. **[HOTS]**

Ans.
$$\Lambda^o_{m(H_2O)} = \lambda^o_{(H^+)} + \lambda^o_{(OH^-)}$$

$$= \lambda^o_{(H^+)} + \lambda^o_{(OH^-)} + \lambda^o_{(Cl^-)} - \lambda^o_{(Cl^-)} + \lambda^o_{(Na^+)} - \lambda^o_{(Na^+)}$$

Rearranging we get

$$\Lambda^o_{m(H_2O)} = \left[\lambda^o_{(H^+)} + \lambda^o_{(Cl^-)}\right] + \left[\lambda^o_{(Na^+)} + \lambda^o_{(OH^-)}\right] - \left[\lambda^o_{(Na^+)} + \lambda^o_{(Cl^-)}\right]$$

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

Thus, the molar conductivity of water at infinite dilution can be determined from the knowledge of $\Lambda^o_{m(HCl)}$, $\Lambda^o_{m(NaOH)}$ and $\Lambda^o_{m(NaCl)}$.

Q. 9. 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 $\lambda^o(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^o(HCOO^-) = 54.6$ S cm^2 mol^{-1}. **[HOTS]**

Ans. $\Lambda^o_m(HCOOH) = \lambda^o_{H^+} + \lambda^o_{HCOO^-} = 349.6$ S cm^2 $mol^{-1} + 54.6$ S cm^2 mol^{-1}

$$\Lambda^o_m = 404.2\ S\ cm^2\ mol^{-1}$$

$$\Lambda^c_m = 46.1\ S\ cm^2\ mol^{-1}\ (Given)$$

$$\therefore \quad \alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{46.1}{404.2} = 0.114$$

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

Initial conc.	c mol L^{-1}	0	0
Conc. at equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114} = \mathbf{3.67 \times 10^{-4}}$$

Q. 10. **If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?** **[*HOTS*]**

Ans. Q (coulomb) = I (ampere) × t (s) = (0.5 ampere) (2 × 60 × 60 s) = 3600 C

A flow of 96500 C is equivalent to the flow of 1 mole of electrons, *i.e.*, 6.02 × 10^{23} electrons

$\therefore$ 3600 C is equivalent to flow of electrons = $\dfrac{6.02 \times 10^{23}}{96500} \times 3600 = \mathbf{2.246 \times 10^{22}}$ **electrons**

Q. 11. **Suggest a list of metals that are extracted electrolytically.**

Ans. Na, Ca, Mg and Al.

Q. 12. **Consider the reaction:**

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

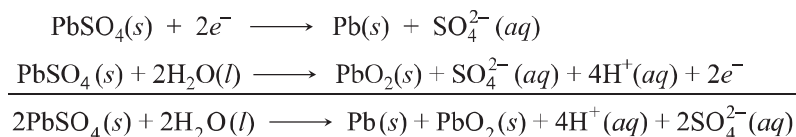**What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?**

Ans. From the given reaction, 1 mole of $Cr_2O_7^{2-}$ ions require

6F = 6 × 96500 C = 579000 C of electricity for reduction to Cr^{3+} ion.

Q. 13. **Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.**

Ans. During recharging, electrical energy is supplied to the cell from an external source. The reactions are reverse of those that takes place during discharge.

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

Q. 14. **Suggest two materials other than hydrogen that can be used as fuels in fuel cells.**

Ans. Methyl alcohol and methane.

Q. 15. **Explain how rusting of iron is envisaged as setting up of an electrochemical cell.**

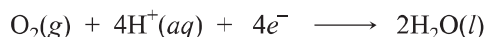**Ans.** The water layer present on the surface of iron dissolves acidic oxides of air like CO_2 to form acids which dissociate to give H^+ ions.

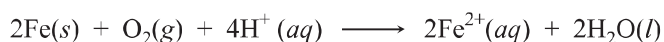$$H_2O + CO_2 \longrightarrow H_2CO_3, \quad H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$
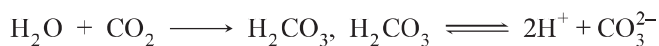
In the presence of H^+ ions, iron starts losing electrons at some spot to form ferrous ions. Hence, this spot acts as the anode:

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

The electrons thus released move through the metal to reach another spot where H^+ ions and the dissolved oxygen gain these electrons and reduction reaction takes place. Hence, this spot acts as the cathode:

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

The overall reaction is given as:

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

Therefore, an electrochemical cell is set up on the surface.

Ferrous ions are further oxidised by the atmospheric oxygen to ferric ions which combine with water molecules to form hydrated ferric oxide, $Fe_2O_3 . xH_2O$, which is rust.
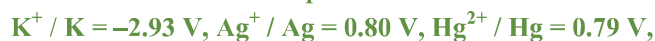
Electrochemistry

NCERT Textbook Exercises

Q. 1. Arrange the following metals in the order in which they displace each other from the solution of their salts.

<p align="center">**Al, Cu, Fe, Mg and Zn**</p>

Ans. Mg, Al, Zn, Fe, Cu.

Q. 2. Given the standard electrode potentials

$K^+ / K = -2.93$ V, $Ag^+ / Ag = 0.80$ V, $Hg^{2+} / Hg = 0.79$ V,

$Mg^{2+} / Mg = -2.37$ V, $Cr^{3+} / Cr = -0.74$ V

Arrange these metals in their increasing order of reducing power. **[CBSE (AI) 2010]**

Ans. Lower the reduction potential, more easily it is oxidised and hence greater is the reducing power. Therefore, the increasing order of reducing power is Ag < Hg < Cr < Mg < K.
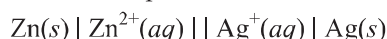
Q. 3. Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

   (*i*) Which of the electrode is negatively charged?

   (*ii*) The carriers of the current in the cell.
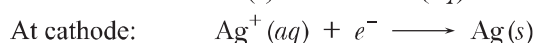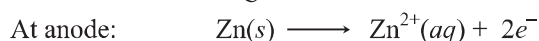
   (*iii*) Individual reaction at each electrode.
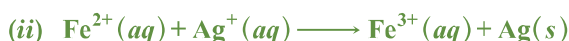
Ans. The cell will be represented as:

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

   (*i*) Anode (zinc electrode) will be negatively charged.

   (*ii*) Electrons and ions.

   (*iii*) The reaction occurring

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

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

Q. 4. Calculate the standard cell potentials of galvanic cell in which the following reactions take place:

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

   (*ii*) $Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Given: $E^o_{Cr^{3+}/Cr} = -0.74$ V, $E^o_{Cd^{2+}/Cd} = -0.40$ V,

$E^o_{Ag^+/Ag} = 0.80$ V, $E^o_{Fe^{3+}/Fe^{2+}} = 0.77$ V

Calculate $\Delta_r G^\circ$ and equilibrium constant of the reactions.

Ans.   (*i*) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.40$ V $- (-0.74$ V$) = +\mathbf{0.34}$ **V**

$\Delta_r G^\circ = -nFE^o_{cell} = -6 \text{ mol} \times 96500 \text{ C mol}^{-1} \times 0.34$ V

$= -196860 \text{ C V mol}^{-1} = -196860 \text{ J mol}^{-1}$

$= \mathbf{-196.86}$ **kJ mol^{-1}**

$\Delta_r G^\circ = -2.303 \, RT \log K_c$

$-196860 = -2.303 \times 8.314 \times 298 \log K_C$ or $\log K_c = 34.5014$

$K_c = $ Antilog $34.5014 = \mathbf{3.172 \times 10^{34}}$

  (*ii*) $E^o_{cell} = +0.80$ V $- 0.77$ V $= +\mathbf{0.03}$ **V**

$\Delta_r G^\circ = -nFE^o_{cell} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03$ V$)$

$= -2895 \text{ CV mol}^{-1} = -2895 \text{ J mol}^{-1} = \mathbf{-2.895}$ **kJ mol^{-1}**

$\Delta_r G^\circ = -2.303 \, RT \log K_C$

$-2895 = -2.303 \times 8.314 \times 298 \times \log K_C$

  or $\log K_c = 0.5074$

  or $K_c = $ Antilog $(0.5074) = \mathbf{3.22}$

Q. 5. Write the Nernst equation and emf of the following cells at 298 K:

    (i) $Mg(s) \mid Mg^{2+} (0.001 \text{ M}) \parallel Cu^{2+} (0.0001 \text{ M}) \mid Cu(s)$

    (ii) $Fe(s) \mid Fe^{2+} (0.001 \text{ M}) \parallel H^+ (1 \text{ M}) \mid H_2(g) \text{ (1 bar)} \mid Pt(s)$

    (iii) $Sn(s) \mid Sn^{2+} (0.050 \text{ M}) \parallel H^+ (0.020 \text{ M}) \mid H_2(g) \text{ (1 bar)} \mid Pt(s)$

    (iv) $Pt(s) \mid Br^- (0.010 \text{ M}) \mid Br_2(l) \parallel H^+ (0.030) \mid H_2(g) \text{ (1 bar)} \mid Pt(s)$

Given, $E^0_{Mg^{2+}/Mg} = -2.37 \text{ V}, E^0_{Cu^{2+}/Cu} = +0.34 \text{ V}, E^0_{Fe^{2+}/Fe} = -0.44 \text{ V},$
$E^0_{Sn^{2+}/Sn} = -0.14 \text{ V}, E^0_{1/2Br_2/Br^-} = +1.08 \text{ V}.$

Ans. (i) Cell reaction: $Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu; \ n = 2$

    Nernst equation: $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2} \log \dfrac{[Mg^{2+}]}{[Cu^{2+}]}$

    $\therefore$ $E_{cell} = 0.34 - (-2.37) - \dfrac{0.0591}{2} \log \dfrac{10^{-3}}{10^{-4}} = 2.71 - 0.02955 = \textbf{2.68 V}$

    (ii) Cell reaction: $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2; \ n = 2$

    Nernst equation: $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2} \log \dfrac{[Fe^{2+}]}{[H^+]^2}$

    $\therefore$ $E_{cell} = 0 - (-0.44) - \dfrac{0.0591}{2} \log \dfrac{10^{-3}}{(1)^2}$

    $= 0.44 - \dfrac{0.0591}{2} \times (-3) = 0.44 + 0.0887 = \textbf{0.529 V}$

    (iii) Cell reaction: $Sn + 2H^+ \longrightarrow Sn^{2+} + H_2; \ n = 2$

    Nernst equation: $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2} \log \dfrac{[Sn^{2+}]}{[H^+]^2}$

    $= 0 - (-0.14) - \dfrac{0.0591}{2} \log \dfrac{0.05}{(0.02)^2}$

    $= 0.14 - \dfrac{0.0591}{2} \log 125 = 0.14 - \dfrac{0.0591}{2}(2.0969) = \textbf{0.078 V}$

    (iv) Cell reaction: $2Br^- + 2H^+ \longrightarrow Br_2 + H_2; n = 2$

    Nernst equation: $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2} \log \dfrac{1}{[Br^-]^2 [H^+]^2}$

    $\therefore$ $E_{cell} = (0 - 1.08) - \dfrac{0.0591}{2} \log \dfrac{1}{(0.01)^2 (0.03)^2}$

    $= -1.08 - \dfrac{0.0591}{2} \log (1.111 \times 10^7)$

    $= -1.08 - \dfrac{0.0591}{2}(7.0457)$

    $= -1.08 - 0.208$

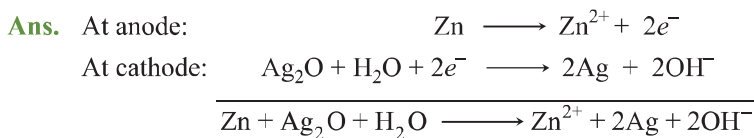 $= \textbf{-1.288 V}$

As E_{cell} is negative, therefore cell reaction will not take place. For the cell to show positive emf cell, representation should be

    $Pt \mid H_2O \text{ (1 bar)} \mid H^+ (0.03 \text{ M}) \parallel Br^- (0.01 \text{ M}) \mid Br_2(l) \mid Pt(s)$
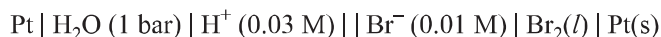
Q. 6. In the button cells widely used in watches and other devices, the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^\circ$ and E^0 for the reaction.

Electrochemistry

Ans. At anode: $$Zn \longrightarrow Zn^{2+} + 2e^-$$
At cathode: $$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$$
$$\overline{Zn + Ag_2O + H_2O \longrightarrow Zn^{2+} + 2Ag + 2OH^-}$$
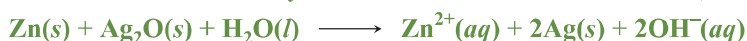
$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$
$$= E^o_{Ag^+/Ag} - E^o_{Zn^{2+}/Zn}$$
$$E^o_{cell} = 0.34 \text{ V} - (-0.76 \text{ V}) = \textbf{1.10 V}$$
$$\Delta G^\circ = -nFE^o_{cell}, \, n = 2$$
$$\Delta G^\circ = -2 \times 96500 \times 1.10$$
$$\boldsymbol{\Delta G^\circ = -2.123 \times 10^5 \text{ J/mol}}$$

Q. 7. **Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.**

Ans. Refer to Basic Concepts Points 5 and 10 for definition.

Variation of Conductivity and Molar Conductivity with Concentration: Conductivity always decreases with the decrease in concentration both, for weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$$G = \frac{\kappa A}{l} = \kappa \quad \text{(both } A \text{ and } l \text{ are unity in their appropriate units}$$
in m or cm).

Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with the area of cross section A and distance of unit length. Therefore,

$$\Lambda_m = \frac{\kappa A}{l} = \kappa$$

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)
$$\Lambda_m = \kappa V$$

Molar conductivity increases with the decrease in concentration. This is because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Q. 8. **The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} Calculate its molar conductivity.**

Ans. $$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \times L^{-1}}{0.20 \text{ mol } L^{-1}} = \textbf{124 S cm}^2 \textbf{ mol}^{-1}$$

Q. 9. **The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10^{-3} S cm^{-1}?**
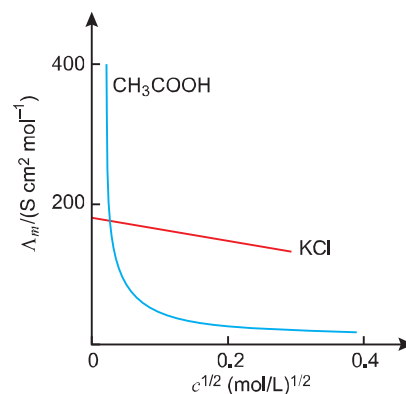
Ans. Conductivity $(\kappa) = \dfrac{1}{\text{Resistance (R)}} \times$ Cell constant

$$\kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}, R = 1500 \, \Omega$$

$$0.146 \times 10^{-3} \text{ S cm}^{-1} = \frac{1}{1500 \, \Omega} \times \text{Cell constant}$$

$$\therefore \qquad \text{Cell constant} = 0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500 \, \Omega$$
$$= 219 \times 10^{-3} \text{ cm}^{-1} = \textbf{0.219 cm}^{-1}$$

Q. 10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

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

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m°.

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

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

Plot between Λ_m and $c^{1/2}$
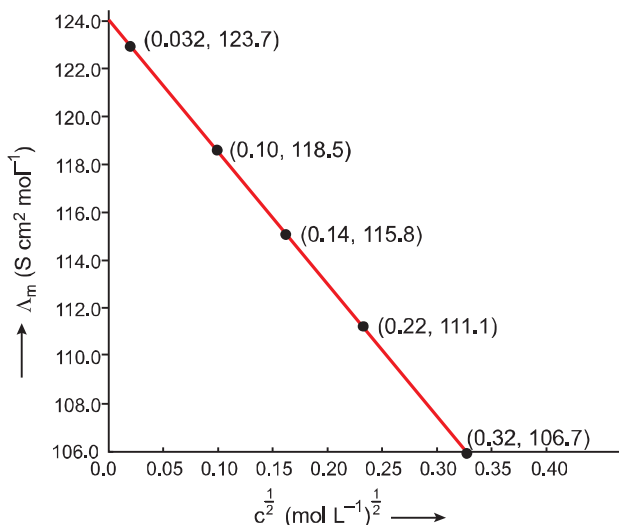
Λ_m^0 = Intercept on the Λ_m axis = **124.0 S cm^2 mol^{-1}**

Q. 11. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1} Calculate its molar conductivity. If Λ_m^o for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant? **[CBSE Delhi 2008]**

Ans. $c = 0.00241$ M, $\kappa = 7.896 \times 10^{-5}$ S cm^{-1}, $\Lambda_m^0 = 390.5$ S cm^2 mol^{-1}

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Substituting the values, we get

$$\Lambda_m = \frac{7.896 \times 10^{-5}\,\text{S cm}^{-1} \times 1000\,\text{cm}^3\,\text{L}^{-1}}{0.00241\,\text{mol L}^{-1}} = \mathbf{32.76\ S\ cm^2\ mol^{-1}}$$

Electrochemistry

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{32.76}{390.5} = 0.084$$

$$\alpha = 8.4\%$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Initial concentration	c	0	0
Concentration at equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K = \frac{0.00241(0.084)^2}{(1-0.084)} = \mathbf{1.86 \times 10^{-5}}$$

Q. 12. **How much charge is required for the following reduction:**

    (*i*) **1 mol of Al^{3+} to Al?**   (*ii*) **1 mol of Cu^{2+} to Cu?**

    (*iii*) **1 mol of MnO_4^- to Mn^{2+}?**   **[*CBSE 2020 (56/5/1)*]**

Ans.   (*i*) $Al^{3+} + 3e^- \longrightarrow Al$

           ∴   Quantity of charge required for reduction of 1 mol of Al^{3+} = 3F

                                                 = 3 × 96500 C = **289500 C**

  (*ii*) $Cu^{2+} + 2e^- \longrightarrow Cu$
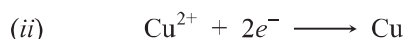
           ∴   Quantity of charge required for reduction of 1 mol of Cu^{2+} = 2F = 2 × 96500 C

                                                   = **193000 C**

  (*iii*) $MnO_4^- \longrightarrow Mn^{2+}$
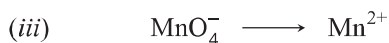
           Oxidation number of Mn changes from +7 to +2.

           ∴   Quantity of charge required = 5F = 5 × 96500 C = **482500 C**

Q. 13. **How much electricity in terms of Faraday is required to produce**

    (*i*) **20.0 g of Ca from molten $CaCl_2$?**

    (*ii*) **40.0 g of Al from molten Al_2O_3?**

Ans.   (*i*) $Ca^{2+} + 2e^- \longrightarrow Ca$

           As, 40 g of Ca, require electricity = 2 F

           ∴   20 g of Ca will require electricity = $\dfrac{20}{40} \times 2 = \mathbf{1\ F}$

  (*ii*) $Al^{3+} + 3e^- \longrightarrow Al$

           As, 1 mol of Al, *i.e.*, 27 g of Al require electricity = 3 F

           ∴   40 g of Al will require electricity = $\dfrac{3}{27} \times 40 = \mathbf{4.44\ F}$

Q. 14. **How much electricity is required in coulomb for the oxidation of**
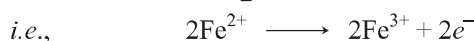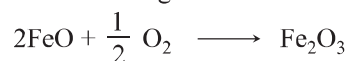
    (*i*) **1 mol of H_2O to O_2**   (*ii*) **1 mol of FeO to Fe_2O_3?**

Ans.   (*i*) The electrode reaction for 1 mol of H_2O is given as

$$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

           ∴   Quantity of electricity required = 2F = 2 × 96500 C = **193000 C**

  (*ii*) The electrode reaction is given as

$$2FeO + \frac{1}{2}O_2 \longrightarrow Fe_2O_3$$

          i.e., $2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^-$

           For the oxidation of 2 moles of FeO, required charge = 2 F

    ∴   For the oxidation 1 mole of FeO, required charge = 1 F = **96500 C**

Q. 15. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? **[CBSE (F) 2014]**

Ans. Quantity of electricity passed $= I \times t = (5 \text{ A}) \times (20 \times 60 \text{ s}) = 6000$ C

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

2×96500 C deposit Ni = 58.7 g

$\therefore$ 6000 C will deposit Ni $= \dfrac{58.7}{2 \times 96500} \times 6000$ g = **1.825 g**

Q. 16. Three electrolytic cells A, B and C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively were connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited? **[CBSE Delhi 2008]**

Ans. $Ag^+ + e^- \longrightarrow Ag$

108 g of Ag is deposited by 96500 C

$\therefore$ 1.45 g of Ag will be deposited by $\dfrac{96500}{108} \times 1.45$ C = 1295.6 C

$$t = \dfrac{Q}{I} = \dfrac{1295.6}{1.50} = \mathbf{863.7 \text{ s}}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

2×96500 C deposit Cu = 63.5 g

$\therefore$ Cu deposited by 1295.6 C $= \dfrac{63.5}{2 \times 96500} \times 1295.6 =$ **0.426 g**

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

2×96500 C deposit Zn = 65.3 g

$\therefore$ Zn deposited by 1295.6 C $= \dfrac{65.3}{2 \times 96500} \times 1295.6 =$ **0.438 g**

Q. 17. Using the standard electrode potentials given below, predict if the reaction between the following is feasible:

   (*i*) Fe^{3+} (*aq*) and I^- (*aq*)   (*ii*) Ag^+ (*aq*) and Cu (*s*)

   (*iii*) Fe^{3+} (*aq*) and Br^- (*aq*)   (*iv*) Ag(*s*) and Fe^{3+} (*aq*)

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

Given standard electrode potentials:

$E^o_{1/2 I_2/I^-} = 0.541$ V, $E^o_{Cu^{2+}/Cu} = +0.34$ V,

$E^o_{1/2 Br_2/Br^-} = +1.090$ V, $E^o_{Ag^+/Ag} = +0.80$ V, $E^o_{Fe^{3+}/Fe^{2+}} = +0.77$ V.

Ans. A reaction is feasible if e.m.f. of the cell reaction is positive.

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

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

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

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

      $E^o_{cell} = E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} = 0.80$ V $- 0.34$ V = **0.46 V (feasible).**

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

      $E^o_{cell} = 0.77$ V $- 1.09$ V = **$-$ 0.32 V (not feasible).**

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

      $E^o_{cell} = 0.77$ V $- 0.80$ V = **$-$ 0.03 V (not feasible).**

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(v) $\dfrac{1}{2}Br_2(aq) + Fe^{2+}(aq) \longrightarrow Br^- + Fe^{3+}$,
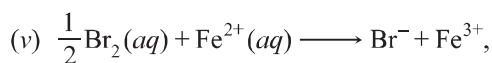
$E^o_{cell} = 1.09\ V - 0.77\ V = \mathbf{0.32\ V\ (feasible)}.$

Q. 18. **Predict the products of electrolysis in each of the following**

    (i) An aqueous solution of $AgNO_3$ with silver electrodes.

    (ii) An aqueous solution of $AgNO_3$ with platinum electrodes.

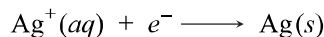   **(iii) A dilute solution of H_2SO_4 with platinum electrodes.**   **[CBSE 2019 (56/3/2)]**

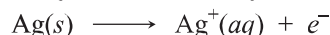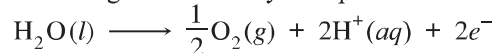   **(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.**   **[CBSE 2020 (56/4/3)]**

Ans. **(i) Electrolysis of aqueous solution of $AgNO_3$ with silver electrodes:**

$$AgNO_3(s) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode: Since, the reduction potential of Ag^+ (+0.80 V) is greater than that of water, (− 0.83 V), Ag^+ will get reduced preferentially and silver metal will get deposited at the cathode. will be deposited as Ag in preference to H^+ ions.
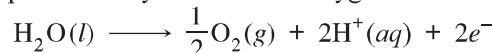
$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

At anode: Following reactions may take place

$$H_2O(l) \longrightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

$$NO_3^-(aq) \longrightarrow NO_3 + e^-$$

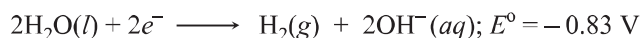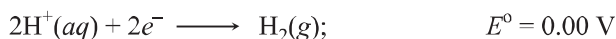$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

Among these reactions, the reduction potential of silver is minimum. Therefore, the silver anode will itself undergo oxidation to form Ag^+ ions which will pass into the solution.
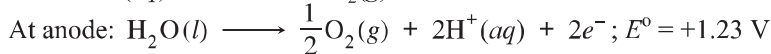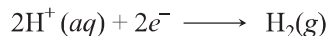
(ii) At cathode: As given in part (i).

At anode: Since the reduction potential of water is less than that of NO_3^- ions, water will get preferentially oxidised and oxygen will be evolved.

$$H_2O(l) \longrightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

(iii) At cathode:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g); \quad\quad\quad E^o = 0.00\ V$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq); E^o = -0.83\ V$$

Since, H^+ ions possess a higher reduction potential as compared to that of water, H^+ will get preferentially reduced and H_2 gas is obtained at the cathode.

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

At anode: $H_2O(l) \longrightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-; E^o = +1.23\ V$

$$SO_4^{2-}(aq) \longrightarrow SO_4 + 2e^-;\ E^o = 2.0\ V$$
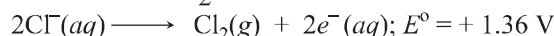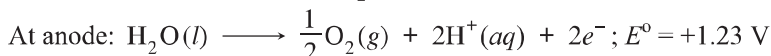
Since, the reduction potential of H_2O is less than that of SO_4^{2-} ions, water will get preferentially oxidised and oxygen will be evolved at the anode.

(iv) At cathode: $2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq); E^o = -0.83\ V$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); E^o = +0.34\ V$$
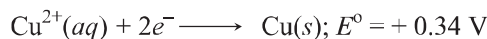
As E^o for Cu^{2+} is greater than H_2O. So, copper metal is deposited at the anode.

At anode: $H_2O(l) \longrightarrow \dfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-; E^o = +1.23\ V$

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-(aq); E^o = +1.36\ V$$

Since E^o value of H_2O is less than Cl^-, water will get preferentially oxidised at anode and O_2 gas will be evolved.