

Chapter 3: Electrochemistry

Electrochemistry is that branch of chemistry which deals with the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Importance of Electrochemistry

1. Production of metals like Na, Mg, Ca and Al.
2. Electroplating.
3. Purification of metals.
4. Batteries and cells used in various instruments.

Conductors

Substances that allow electric current to pass through them are known as conductors.

Metallic Conductors or Electronic Conductors

Substances which allow the electric current to pass through them by the movement of electrons are called metallic conductors, e.g., metals.

Electrolytic Conductors or Electrolytes

Substances which allow the passage of electricity through their fused state or aqueous solution and undergo chemical decomposition are called electrolytic conductors, e.g., aqueous solution of acids, bases and salts.

Electrolytes are of two types:

1. Strong electrolytes

The electrolytes that completely dissociate or ionise into ions are called strong electrolytes. e.g., HCl, NaOH, K_2SO_4

2. Weak electrolytes

The electrolytes that dissociate partially ($\alpha < 1$) are called weak electrolytes, e.g., CH_3COOH , H_2CO_3 , NH_4OH , H_2S , etc.

Electrochemical Cell and Electrolytic

6. Salt bridge	Salt bridge is required	Salt bridge is not required.
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A cell of almost constant emf is called standard cell. The most common is Weston standard cell.

Galvanic cell is also called voltaic cell.

General Representation of an Electrochemical Cell

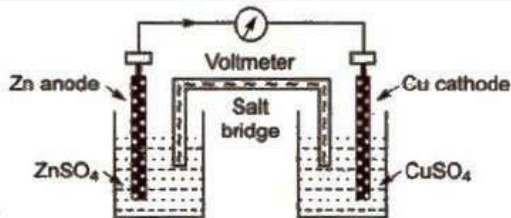
\bar{e}		\downarrow	
$M_1(s) M_1^{n+}(aq)$		$M_2^{n+}(aq) M_2(s)$	
Anode	Salt bridge	Cathode	Cathode
Oxidation half-cell		Reduction half-cell	
	Cathode		Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons	
Reaction	Reduction	Oxidation	
Movement of electrons	Into the cell	Out of cell	

Other features of the electrochemical cell are

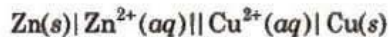
1. There is no evolution of heat.
2. The solution remains neutral on both sides.
3. The reaction and flow of electrons stops after sometime.

Daniell Cell

An electrochemical cell of zinc and copper metals is known as Daniell cell. It is represented as



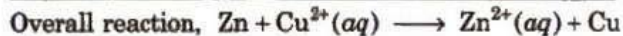
Cell diagram,



LHS oxidation,



RHS reduction,



By convention cathode is represented on the RHS and anode on the LHS.

Function of salt bridge

1. It completes the circuit and allows the flow of current.
2. It maintains the electrical neutrality on both sides. Salt-bridge generally contains solution of strong electrolyte such as KNO_3 , KCl etc. KCl is preferred because the transport numbers of K^{+} and

mentioned.

$E^{\circ}_{\text{red}} = - E^{\circ}_{\text{oxidation}}$

It is not possible to determine the absolute value of electrode potential. For this a reference electrode [NHE or SHE] is required. The electrode potential is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

Standard electrode potential

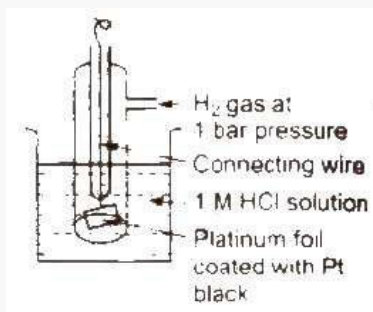
The potential difference developed between metal electrode and solution of ions of unit molarity (1M) at 1 atm pressure and 25°C (298 K) is called standard electrode potential.

It is denoted by E° .

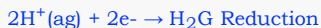
Reference Electrode

The electrode of known potential is called reference electrode. It may be primary reference electrode like hydrogen electrode or secondary reference electrode like calomel electrode.

Standard hydrogen electrode (SHE) Standard hydrogen electrode (SHE), also known as normal hydrogen electrode (NHE), consists of platinum wire, carrying platinum foil coated with finely divided platinum black. The wire is sealed into a glass tube, placed in beaker containing 1 M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. Half-cell is $\text{Pt} | \text{H}_2 (1 \text{ atm}) | \text{H}^+ (1 \text{ M})$



In SHE, at the surface of platinum, either of the following reaction can take place



The electrode potential of SHE has been fixed as zero at all temperatures.

Its main drawbacks are

1. It is difficult to maintain 1 atm pressure of H_2 gas.
2. It is difficult to maintain H^+ ion concentration 1 M.
3. The platinum electrode is easily poisoned by traces of impurities.

Hence, calomel electrodes are conveniently used as reference electrodes, It consists of mercury in contact with $\text{Hg} | \text{Cl}^-$ (calomel) paste in a solution of KCl.

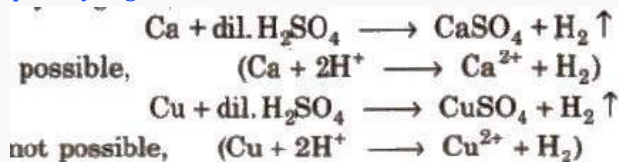
$\text{Co}^{3+} + e^{-}$	\rightarrow	Co^{2+}	1.81
$\text{H}_2\text{O}_2 + 2\text{H}^{+} + 2e^{-}$	\rightarrow	$2\text{H}_2\text{O}$	1.78
$\text{MnO}_4^{-} + 8\text{H}^{+} + 5e^{-}$	\rightarrow	$\text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{Au}^{3+} + 3e^{-}$	\rightarrow	Au(s)	1.40
$\text{Cl}_2(\text{g}) + 2e^{-}$	\rightarrow	2Cl^{-}	1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{+} + 6e^{-}$	\rightarrow	$2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^{+} + 4e^{-}$	\rightarrow	$2\text{H}_2\text{O}$	1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^{+} + 2e^{-}$	\rightarrow	$\text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
$\text{Br}_2 + 2e^{-}$	\rightarrow	2Br^{-}	1.09
$\text{NO}_3^{-} + 4\text{H}^{+} + 3e^{-}$	\rightarrow	$\text{NO}(\text{g}) + 2\text{H}_2\text{O}$	0.97
$2\text{Hg}^{2+} + 2e^{-}$	\rightarrow	Hg_2^{2+}	0.92
$\text{Ag}^{+} + e^{-}$	\rightarrow	Ag(s)	0.80
$\text{Fe}^{3+} + e^{-}$	\rightarrow	Fe^{2+}	0.77
$\text{O}_2(\text{g}) + 2\text{H}^{+} + 2e^{-}$	\rightarrow	H_2O_2	0.68
$\text{I}_2 + 2e^{-}$	\rightarrow	2I^{-}	0.54
$\text{Cu}^{+} + e^{-}$	\rightarrow	Cu(s)	0.52
$\text{Cu}^{2+} + 2e^{-}$	\rightarrow	Cu(s)	0.34

Applications of Electrochemical Series (ECS)

1. The lower the value of E° , the greater the tendency to form cation.



Metals placed below hydrogen in ECS replace hydrogen from dil acids but metals placed above hydrogen cannot replace hydrogen from dil acids.



3. Oxides of metals placed below hydrogen are not reduced by H_2 but oxides of iron and metals placed above iron are reduced by H_2 .

• SnO , PbO , CuO are reduced by H_2

• CaO , K_2O are not reduced by H_2 .

4. Reducing character increases down the series.

5. Reactivity increases down the series.

6. Determination of emf; emf is the difference of reduction potentials of two half-cells.

$$E_{\text{emf}} = E_{\text{RHS}} - E_{\text{LHS}}$$

If the value of emf is positive, then reaction take place spontaneously, otherwise not.

7. Greater the reduction potential of a substance, oxidising power. (e.g., $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$)

8. A negative value of standard reduction potential shows that it is the site of oxidation.

9. Oxides of metals having $E^\circ_{\text{red}} \geq 0.79$ will be decomposed by heating to form O_2 and metal.



$$(E^\circ_{\text{Hg}^{2+}/\text{Hg}} = 0.79\text{V})$$

Nernst Equation

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

$$M^{n+} + ne^- \longrightarrow M$$
$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}]}$$
$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.0591}{n} \log \left[\frac{1}{[M^{n+}]} \right]$$

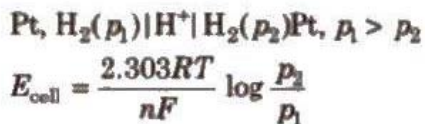
For an electrochemical cell,

Relationship between free energy change and equilibrium constant

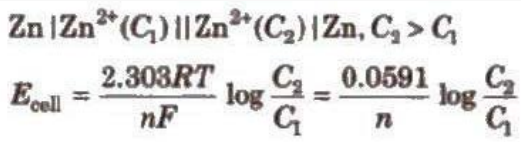
$$\Delta G^\circ = -2.303RT \log K_c$$

Concentration Cells

(i) Electrode concentration cells Two hydrogen electrodes or different pressures are dipped in the same solution of electrolyte, e.g.,



(ii) Electrolyte concentration cells Electrodes are the same but electrolyte solutions have different concentrations, e.g.,



Conductance (G)

It is the ease of flow of electric current through the conductor. It is reciprocal of resistance (R).

$$G = (1/R), \text{ units } \text{ohm}^{-1} \text{ mhos or } \Omega^{-1}$$

Specific Conductivity (K)

It is the reciprocal of specific resistance.

$$\kappa = \frac{1}{\rho} = \frac{l}{R \cdot a} = G \times \frac{l}{a} = G \times \text{cell constant } (G^*)$$
$$\left(\frac{l}{a} = \text{cell constant} \right)$$

$$\text{Units of } \kappa = \Omega^{-1} \text{cm}^{-1}$$
$$= \text{S cm}^{-1} (\Omega^{-1} = \text{S i.e., Siemens})$$

Unit of cell constant is cm^{-1} or m^{-1} .

Specific conductivity decreases on dilution. This is because concentration of ions per cc decreases upon dilution.

Molar Conductivity (Λ_m)

The conductivity of all the ions produced when 1 mole of an electrolyte is dissolved in V mL of solution is known as molar conductivity.

It is related to specific conductance as

$$\Lambda_m = (k \times 1000/M)$$

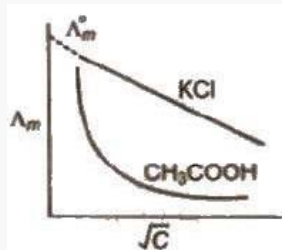
where, M = molarity.

conductivity (molar as well as equivalent) .

ii) Concentration of the solution

The concentrated solutions of strong electrolytes have Significant interionic attractions, which reduce the speed of ions and lower the value of Λ_m and Λ_{eq} .

The dilution decreases such attractions and increase the value of Λ_m and Λ_{eq} .



The limiting value, Λ_m^0 or Λ_{eq}^0 , (the molar conductivity at zero concentration (or at infinite dilution) can be obtained extrapolating the graph.

In case of weak electrolytes, the degree of ionisation increases dilution which increases the value of Λ_m and Λ_{eq} . The limiting value Λ_m^0 cannot be obtained by extrapolating the graph. ~ limiting value, Λ_m^0 , for weak electrolytes is obtained by Kohlrausch law.

(iii) Temperature The increase of temperature decreases inter-ionic attractions and increases kinetic energy of ions and their speed. Thus, Λ_m and Λ_{eq} increase with temperature.

Kohlrausch' s Law

At infinite dilution, the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions, e.g., for A_xB_y .

$$\Lambda_m^0 (A_xB_y) = x\Lambda_{A^+}^0 + y\Lambda_{B^-}^0$$
$$\Lambda_{eq}^0 = \Lambda_{A^+}^0 + \Lambda_{B^-}^0$$

Applications

(i) Determination of equivalent/molar conductivities of weak electrolytes at infinite dilution, e.g.,

$$\Lambda_{CH_3COOH}^{\infty} = \Lambda_{CH_3COONa}^{\infty} + \Lambda_{HCl}^{\infty} - \Lambda_{NaCl}^{\infty}$$
$$\Lambda_{NH_4OH}^{\infty} = \Lambda_{NH_4Cl}^{\infty} + \Lambda_{NaOH}^{\infty} - \Lambda_{NaCl}^{\infty}$$

(ii) Determination of degree of dissociation (α) of an electrolyte at a given dilution.

$$\alpha = \frac{\text{molar conductance at concentration 'C'}}{\text{molar conductance at infinite dilution}} = \frac{\Lambda_m^C}{\Lambda_m^{\infty}}$$

anode.

4. When two or more ions compete at the electrodes, the ion with higher reduction potential gets liberated at the cathode while the ion with lower reduction potential at the anode.

For metals to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called over voltage or bubble voltage.

How to Predict the Products of Electrolysis?

When an aqueous solution of an electrolyte is electrolysed, if the cation has higher reduction potential than water (-0.83 V), cation is liberated at the cathode (e.g., in the electrolysis of copper and silver salts) otherwise H₂ gas is liberated due to reduction of water (e.g., in the electrolysis of K, Na, Ca salts, etc.)

Similarly if anion has higher oxidation potential than water (- 1.23 V), anion is liberated (e.g., Br⁻), otherwise O₂ gas is liberated due to oxidation of water (e.g., in case of F⁻, aqueous solution of Na₂SO₄ as oxidation potential of SO₄²⁻ is - 0.2 V).

Discharge potential is defined as the minimum potential that must be applied across the electrodes to bring about the electrolysis and subsequent discharge of the ion on the electrode.

Faraday's Laws of Electrolysis

1. First law

The amount of the substance deposited or liberated at cathode directly proportional to the quantity of electricity passed through electrolyte.

$$W \propto I \times t \quad \text{or} \quad W = I \times t \times Z = Q \times Z$$

• I current in amp, t = time in sec,

• Q = quantity of charge (coulomb)

• Z is a constant known as electrochemical equivalent.

When I = 1 amp, t = 1 sec then Q = 1 coulomb, then w = Z.

Thus, electrochemical equivalent "Z" the amount of the substance deposited or liberated by passing 1A current for 1 sec (i.e., 1 coulomb, I x t = Q)

2. Second law

When the same quantity of electricity is passed through different electrolytes, the amounts of the substance deposited or liberated at the electrodes are directly proportional to their equivalent weights, Thus,



Anode reaction,



Cell potential 1.25 V to 1.5 V

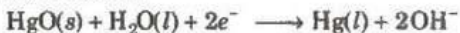
(ii) Mercury cell

Anode-Zn-Hg amalgam

Cathode-Paste of (HgO + C)

Electrolyte-Moist paste of KOH-ZnO

Cathode reaction,



Anode reaction,



Net reaction,



Cell potential 1.35 V

Secondary Batteries

These cells can be recharged and can be used again and again, e.g.,

(i) Lead Storage battery

Anode-Spongy lead

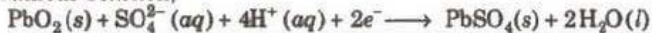
Cathode-Grid of lead packed with PbO₂

Electrolyte-38% H₂SO₄ by mass

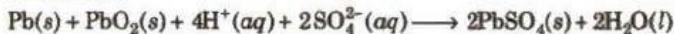
Anode reaction,



Cathode reaction,



Net reaction,



When recharged the cell reactions are reversed.

(ii) Nickel-cadmium storage cell

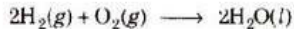
Anode-Cadmium

Cathode-Metal grid containing NiO₂ Electrolyte-KOH solution

Anode reaction,



Net reaction,



EMF of the cell 1 V.

Thermodynamic efficiency of a fuel cell,

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$$

Corrosion

Slow formation of undesirable compounds such as oxides, sulphides or carbonates at the surface of metals by reaction with moisture and other atmospheric gases is known as orrosion.

Factors Affecting Corrosion

1. Reactivity of metals
2. Presence of moisture and atmospheric gases like CO_2 , SO_2 , etc.
3. Presence of impurities
4. Strains in the metal
5. Presence of electrolyte

Rusting of Iron-Electrochemical Theory

An electrochemical cell, also known as corrosion cell, is developed at the surface of iron.

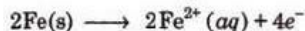
Anode- Pure iron

Cathode-Impure surface

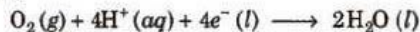
Electrolyte,



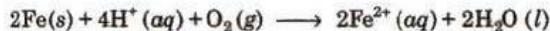
Anode reaction,



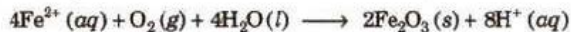
Cathode reaction,



Net reaction,



At surface,



Rusting of iron can be prevented by the following methods :

1. Barrier protection through coating of paints or electroplating.
2. Through galvanisation or coating of surface with tin metal.
3. By the use of antirust solutions (bis phenol).
4. By cathodic protection in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidised.

SUMMARY

- Oxidation:
It is defined as a loss of electrons while reduction is defined as a gain of electrons.
- In a redox reaction, both oxidation and reduction reaction takes place simultaneously.
- Direct redox reaction:
In a direct redox reaction, both oxidation and reduction reactions take place in the same vessel. Chemical energy is converted to heat energy in a direct redox reaction.
- Indirect redox reaction:
In indirect redox reactions, oxidation and reduction take place in different vessels.
- In an indirect redox reaction, chemical energy is converted into electrical energy. The device which converts chemical energy into electrical energy is known as an electrochemical cell.
- In an electrochemical cell:
 - a) The half-cell in which oxidation takes place is known as oxidation half-cell
 - b) The half-cell in which reduction takes place is known as reduction half-cell.
 - c) Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged.
 - d) Transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction.
 - e) An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt.
 - f) A salt bridge is a U shaped tube containing an inert electrolyte in agar-agar and gelatine.
- Salt bridge:
A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.
- Representation of an electrochemical cell:
 - a) Anode is written on the left while the cathode is written on the right.
 - b) Anode represents the oxidation half-cell and is written as:
Metal/Metal ion (Concentration)
 - c) Cathode represents the reduction half-cell and is written as:
Metal ion (Concentration)/Metal
 - d) Salt bridge is indicated by placing double vertical lines between the anode and the cathode
 - e) Electrode potential is the potential difference that develops between the electrode and its electrolyte. The separation of charges at the equilibrium state

results in the potential difference between the metal and the solution of its ions. It is the measure of tendency of an electrode in the half cell to lose or gain electrons.

- Standard electrode potential:

When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential. It is denoted as E^\ominus .

- According to the present convention, standard reduction potentials are now called standard electrode potential.

- Types of electrode potential:

There are 2 types of electrode potentials namely,

- a) Oxidation potential
- b) Reduction potential

- Oxidation potential:

It is the tendency of an electrode to lose electrons or get oxidized.

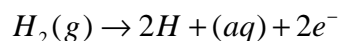
- Reduction potential:

It is the tendency of an electrode to gain electrons or get reduced.

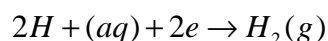
- Oxidation potential is the reverse of reduction potential.
- The electrode having a higher reduction potential have higher tendency to gain electrons and so it acts as a cathode whereas the electrode having a lower reduction potential acts as an anode.
- The standard electrode potential of an electrode cannot be measured in isolation.
- According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures.
- Reference electrode:
Standard calomel electrode can also be used as a reference electrode.
- SHE:

Standard hydrogen electrode consists of a platinum wire sealed in a glass tube and carrying a platinum foil at one end. The electrode is placed in a beaker containing an aqueous solution of an acid having 1 Molar concentration of hydrogen ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at 298 K. The oxidation or reduction takes place at the Platinum foil. The standard hydrogen electrode can act as both anode and cathode.

- If the standard hydrogen electrode acts as an anode:



- If the standard hydrogen electrode acts as a cathode:



- In the electrochemical series, various elements are arranged as per their standard reduction potential values.
- A substance with higher reduction potential value means that it has a higher tendency to get reduced. So, it acts as a good oxidising agent.

- A substance with lower reduction potential value means that it has a higher tendency to get oxidised. So, it acts as a good reducing agent.
- The electrode with higher reduction potential acts as a cathode while the electrode with a lower reduction potential acts as an anode.
- The potential difference between the 2 electrodes of a galvanic cell is called cell potential and is measured in Volts.
- The cell potential is the difference between the reduction potential of cathode and anode.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

- Cell potential is called the electromotive force of the cell (EMF) when no current is drawn through the cell.
- Nernst studied the variation of electrode potential of an electrode with temperature and concentration of electrolyte.
- Nernst formulated a relationship between standard electrode potential E^\ominus and electrode potential E .

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

$$E = E^\ominus - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \text{ (At 298k)}$$

- Electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.
- Nernst equation when applied to a cell, it helps in calculating the cell potential.

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{2.303RT}{nF} \log \frac{[\text{Anode ion}]}{[\text{Cathode ion}]}$$

- At equilibrium, cell potential E_{cell} becomes zero.
- Relationship between equilibrium constant K_c and standard cell potential E^\ominus_{cell} :

$$E_{\text{cell}}^\ominus = \frac{0.059}{n} \log K_c \text{ (At 298K)}$$

- Work done by an electrochemical cell is equal to the decrease in Gibbs energy

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

- The substances which allow the passage of electricity through them are known as conductors.
- Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.
- The resistance of any object is directly proportional to its length l and inversely proportional to its area of cross section A .

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

Where ρ is called specific resistance or resistivity.

- The SI unit of specific resistivity is ohm metre.
- The inverse of resistance is known as conductance, G
- Unit of conductance is ohm⁻¹ or mho. It is also expressed in Siemens denoted by S.
- The inverse of resistivity is known as conductivity. It is represented by the symbol κ .
- The SI unit of conductivity is Sm⁻¹. But it is also expressed in Scm⁻¹.
- Conductivity = Conductance \times Cell constant
- For measuring the resistance of an ionic solution, there are 2 problems:
 - a) Firstly, passing direct current changes the composition of the solution
 - b) Secondly, a solution cannot be connected to the bridge like a metallic wire or a solid conductor.

- Conductivity cell:

The problem of measuring the resistance of an ionic solution can be resolved by using a source of alternating current and the second problem is resolved by using a specially designed vessel called conductivity cell.

- A conductivity cell consists of 2 Pt electrodes coated with Pt black. They have area of cross section A and are separated by a distance 'l'. Resistance of such a column of solution is given by the equation:

$$R = \rho \frac{l}{A} = \frac{1}{k} \frac{l}{A}$$

Where $\frac{l}{A}$ is called cell constant and is denoted by the symbol G^*

- Molar conductivity of a solution:

It is defined as the conducting power of all the ions produced by dissolving 1 mole of an electrolyte in solution.

$$\text{Molar conductivity } \wedge_m = \frac{k \times 1000}{M}$$

Where κ = Conductivity and M is the molarity Unit of Molar conductivity is Scm² mol⁻¹

- Equivalent conductivity:

It is the conductivity of all the ions produced by dissolving one gram equivalent of an electrolyte in solution. Unit of equivalent conductivity is S cm² (g equiv)⁻¹

$$\text{Equivalent conductivity } \wedge_e = \frac{k \times 1000}{N}$$

- Kohlrausch's Law of independent migration of ions:

According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions.

- If the limiting molar conductivity of the cations is denoted by λ_+^0 and that of the anions by λ_-^0 , then the limiting molar conductivity of electrolyte is:

$$\text{Molar conductivity, } \wedge_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$$

Where v₊ and v₋ are the number of cations and anions per formula of electrolyte

- Degree of dissociation:

It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution. It is denoted by α .

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

- Dissociation constant:

$k_a = \frac{ca^2}{1-a}$ Where K_a is acid dissociation constant, 'c' is concentration of electrolyte, α is degree of ionization.

- Faraday constant:

It is equal to charge on 1 mol of electrons. It is equal to 96487 C mol⁻¹ or approximately equal to 96500 C mol⁻¹.

- Faraday's first law of electrolysis:

The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed.

- Faraday's second law of electrolysis:

If same charge is passed through different electrolytes, the mass of substance deposited will be proportional to their equivalent weights.

- Products of electrolysis:

The products of electrolysis depend upon

a) The nature of electrolyte being electrolyzed and the nature of electrodes. If electrode is inert like platinum or gold, they do not take part in chemical reaction i.e. they neither lose nor gain electrons. If the electrodes are reactive then they will take part in chemical reaction and products will be different as compared to inert electrodes.

b) The electrode potentials of oxidizing and reducing species. Some of the electrochemical processes although feasible but slow in their rates at lower voltage, these require extra voltage, i.e. over voltage at which these processes will take place. The products of electrolysis also differ in molten state and aqueous solution of electrolyte.

- Primary cells:

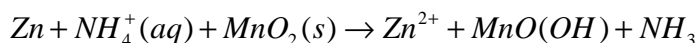
A primary cell is a cell in which electrical energy is produced by the reaction occurring in the cell, e.g. Daniel cell, dry cell, mercury cell. It cannot be recharged.

- Dry Cell:

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

At cathode $MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH) + NH_3$

The net reaction:

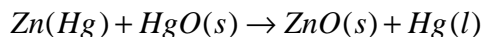


- Mercury Cell.

The electrolyte is a paste of KOH and ZnO.



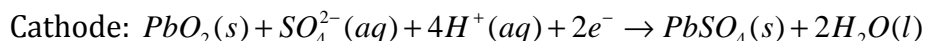
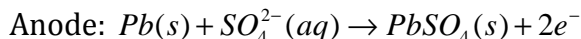
The net reaction:



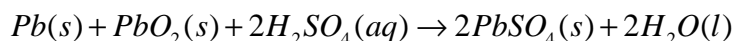
- Secondary cells:

Those cells which are used for storing electricity, e.g., lead storage battery, nickel – cadmium cell. They can be recharged.

- Lead storage battery:



The overall cell reaction consisting of cathode and anode reactions is:



On recharging the battery, the reaction is reversed.

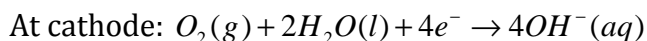
- Nickel cadmium cell:

It is another type of secondary cell which has longer life than lead storage cell but more expensive to manufacture.

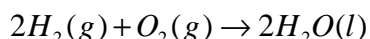
The overall reaction during discharge is



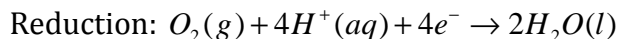
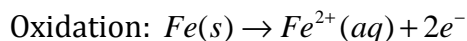
- Fuel cells:



Overall reaction:



- Corrosion:



- Galvanization:

It is a process of coating zinc over iron so as to protect it from rusting.

- Cathodic protection:

Instead of coating more reactive metal on iron, the use of such metal is made as sacrificial anode.