

Electrochemistry

4.1 Introduction

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.

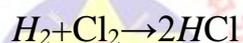
The redox reaction are the basis of the generation of electricity by chemical reaction and the production of chemical reaction by electricity.

4.2 Redox Reaction

The redox reaction are those in which oxidation and reduction always occur simultaneously.

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction

A redox reaction is a reaction that involves a change in oxidation state of one or more elements. When a substance loses an electron, its oxidation state increases; thus, it is oxidized. When a substance gains an electron, its oxidation state decreases, thus being reduced. For example, for the redox reaction



can be rewritten as follows:

- Oxidation: $H_2 \rightarrow 2H^+ + 2e^-$
- Reduction: $Cl_2 + 2e^- \rightarrow 2Cl^-$
- Overall Reaction: $H_2 + Cl_2 \rightarrow 2H^+ + 2Cl^-$

Oxidation is the loss of electrons, whereas reduction is gain of electron of electrons, as illustrated in the respective reactions above. The species being oxidized is also known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. In this case, H_2 is being oxidized (and is the reducing agent), while Cl_2 is being reduced (and is the oxidizing agent).

Rules for calculating oxidation Number

1. Free elements have an oxidation state of 0. (e.g., He, N_2 , O_2 has an oxidation state of 0)
2. The oxidation state of one atom ion must equal the net charge. (Ex: F^- oxidation state is -1, K^+ oxidation state is +1)
3. The sum of the oxidation state has to equal the total net charge for a compound. (Ex: MnO_4^- has a net charge of -1, $Mn(+7)O_4(-8) = -1$)
4. The alkali metals (Group I elements) have an oxidation state of +1. (EX: Li_2O , $Li = +1$)
5. The alkaline earth metals (Group II elements) always have an oxidation state of +2. (Ex: CaO , $Ca = +2$)
6. Oxygen has an oxidation state of -2 in a compound
7. Fluorine has an oxidation state of -1 in a compound
8. Hydrogen has an oxidation state of +1 in a compound.

9. Transition metals and other metals may have more than one common ionic charge. (EX: Chromium's common ionic charges are Cr^{+2} and Cr^{+3})

Balancing Redox Reactions

Method 1: Oxidation Number Method

- Step 1: Assign oxidation numbers to each atom.
- Step 2: Determine the net change in charge to determine the ratio of atoms
- Step 3: Use the ratio to eliminate the net charge change
- Step 4: Use the ratio as coefficients for the elements
- Step 5: Add H^+ (under acidic conditions), OH^- (under basic conditions), and H_2O to balance charges.

Method 2: Half-Reaction Method

- Step 1: Determine oxidation numbers for each atom
- Step 2: Use oxidation numbers to determine what is oxidized and what is reduced.
- Step 3: Write a half-reaction for reduction
- Step 4: Write a half-reaction for oxidation
- Step 5: Balance all elements except H and O
 - if have acid redox reaction: Balance the O using H_2O , balance the H using protons
 - if have base redox reaction: Balance O using OH^-
- Step 6: Add up the charge on each side
- Step 7: Balance the charges by adding electrons
- Step 8: Multiply the half-reactions by factors that cancel out electrons
- Step 9: Add the two half-reactions back together to eliminate out intermediates

4.3 Conductance in electrolytic solutions

The Substances that allow the flow of electricity through them are called conductors. The conductors are classified into two types depending upon the mechanism of transfer of electrons.

i)Electronic conductors

The conductors through which the conduction of electricity occurs by the direct flow of electron under the influence applied potential are known as electronic conductor.

Examples – solid and molten metals such as aluminium copper etc.

ii)Electrolytic conductors

The conductors in which conduction takes place by the migration of positive and negative ions are known as electrolytic conductors.

Examples – the solutions of ionic salts, strong and weak acid and bases.

Conductivity

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

$G = (1/R)$, units ohm⁻¹ mhos or Ω^{-1}

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

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

The proportionality constant ρ is called resistivity of the conductor . if $l = 1\text{m}$ and $a = 1\text{m}^2$ then $R = \rho$. Hence the resistivity of conductor is defined as the resistance of the conductor ie 1m long and 1m^2 in cross – sectional area. The units of ρ are Ωm

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

The electrical conductance of a material is directly proportional to its area of cross section and inversely proportional to its length. Thus

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

$$K = G \frac{l}{a} = \frac{1}{R} \cdot \frac{l}{a}$$

Where K is proportionality constant called conductivity of conductor.

$$K = \frac{1}{\rho}$$

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.

Its units are $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ or $\text{S cm}^2 \text{mol}^{-1}$.

Equivalent conductivity (Λ_{eq})

The conducting power of all the ions produced when 1 g-equivalent of an electrolyte is dissolved in V mL of solution, is called equivalent conductivity. It is related to specific conductance as

$$\Lambda_m = (k \times 1000/N) \quad \text{where. } N = \text{normality.}$$

Its units are $\text{ohm}^{-1} \text{cm}^2 (\text{equiv}^{-1})$ or $\text{mho cm}^2 (\text{equiv}^{-1})$ or $\text{S cm}^2 (\text{g-equiv}^{-1})$

Debye -Huckel Onsagar equation It gives a relation between molar conductivity, Λ_m at a particular concentration and molar conductivity Λ_m^∞ at infinite dilution.

$\Lambda_m = \Lambda_m^\infty - b\sqrt{C}$ where, b is a constant. It depends upon the nature of solvent and temperature.

Factors Affecting Conductivity

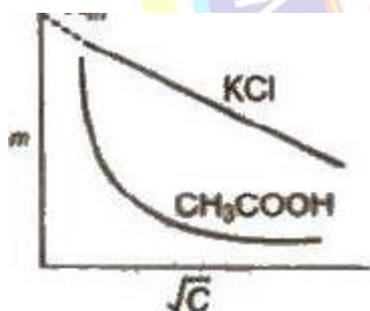
(i) **Nature of electrolyte** -The strong electrolytes like KNO_3 , KCl , NaOH , etc. are completely ionised in aqueous solution and have high values of conductivity (molar as well as equivalent).

The weak electrolytes are ionised to a lesser extent in aqueous solution and have lower values of 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^∞ or Λ_{eq}^∞ . (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^∞ cannot be obtained by extrapolating the graph. ~limiting value, Λ_m^∞ , 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 cation and anions,

The law states that at infinite dilution , each ion migrates independently of its co – ion and make its own contribution to the total molar conductivity of an electrolyte irrespective of the nature of the other ion with which it is associated

e.g., for A_xB_y

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

$$\Lambda_{eq}^0 = \Lambda_{A^+}^0 + \Lambda_{B^-}^0$$

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 solution can be

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

The dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated by using the formula

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

where, α is the degree of dissociation of the electrolyte.

(iii) Salts like $BaSO_4$, $PbSO_4$, $AgCl$, $AgBr$ and AgI which do not dissolve to a large extent in water are called sparingly soluble salts.

The solubility of a sparingly soluble salt can be calculated as ;

$$\Lambda_m^0 = \frac{\kappa \times 1000}{\text{solubility (in mol L}^{-1}\text{)}}$$

$$\text{Solubility (in mol L}^{-1}\text{)} = \frac{\kappa \times 1000}{\Lambda_m^0}$$

4.4 Electrolysis

An electrolysis is therefore defined as a process in which an electric current is used to bring about a chemical reaction or a process in which an electrical energy is converted into a chemical energy.

1. In electrolytic cell both oxidation and reduction takes place in the same cell.
2. Anode is positively charged and cathode is negatively charged, In electrolytic cell.
3. During electrolysis of molten electrolyte, cations are liberated at cathode. while anions at

the 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.

Faraday's Laws of Electrolysis

1. First law

It states that the amount of substance that undergoes oxidation or reduction at each electrode is directly proportional to the amount of electricity that passes through the cell. The amount of the substance deposited or liberated at cathode directly proportional to the quantity of electricity passed through electrolyte.

$$W \propto I \times t = I \times t \times Z = Q \times Z$$

- 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, $I \times t = Q$)

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,

$$\frac{\text{Mass of A}}{\text{Mass of B}} = \frac{\text{eq. wt. of A}}{\text{eq. wt. of B}}$$
$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \Rightarrow \frac{Z_1 Q}{Z_2 Q} = \frac{E_1}{E_2}$$

Hence, electrochemical equivalent \propto equivalent weight

Quantitative aspects of faradays laws of electrolysis

Faradays first law of electrolysis

The mass of the reactant consumed or of the product formed at an electrode during electrolysis is calculated by using the stoichiometry of the half reaction and the molar mass of the substance . The following procedure is used in the calculations ;

(i) Quantity of electricity passed; The quantity of electricity passed through a cell is calculated by measuring the quantity of electric current I passed through the cell and the time t of the passage of current . The quantity of electricity Q is given by

$$Q (C) = I (A) \times t (s)$$

(ii) Number of electrons passed in moles; The charge of one mole electrons is 96500C. Hence, number of moles of electrons actually passed = $Q (C) / 96500 (C / \text{mole})$

(iii) Number of moles of product formed; The balanced equation of the half reaction indicates the number of moles electrons used and number of moles of product formed. From these quantities the number of moles of product actually formed can be calculated as

Number of moles of product formed = number of moles electrons actually passed \times mole ratio

Where mole ratio =
$$\frac{\text{moles of product formed in half reaction}}{\text{moles of electrons required in half reaction}}$$

(iv) Mass of product formed ; Mass of product formed = number of moles of product formed \times its molar mass. From the above steps, the following general formula can be used to calculate the mass of the substance produced.

(i) Moles of the substance produced =
$$\frac{I (A) \times t (s)}{96500 (C / \text{mol e})} \times \text{mole ratio}$$

(ii) Mass of the substance produced =
$$\frac{I (A) \times t (s) \times \text{mole ratio} \times \text{molar mass of the substance}}{96500 (C / \text{mol e})}$$

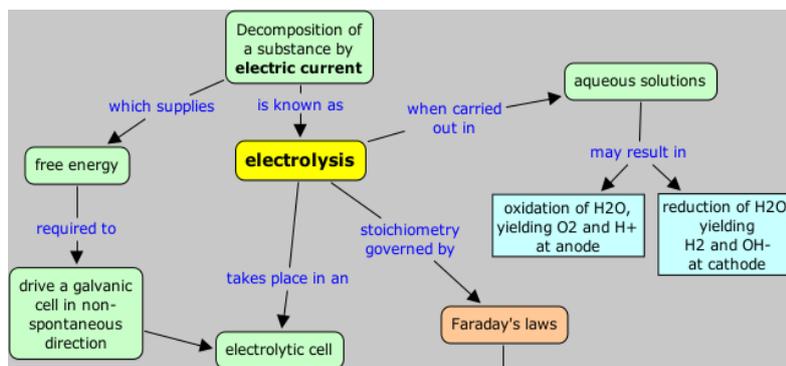
Faraday`s second law of electrolysis

Two cells containing different electrolytes are connected in series. The same quantity of electricity that is the same number of moles of electrons are actually passed through them.

Moles of A produced in one cell = moles of electrons actually passed \times mole ratio of A half reaction.

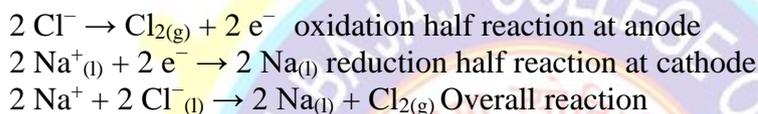
Moles of B produced in other cell = moles of electrons actually passed \times mole ratio of B half reaction.

$$\frac{\text{moles of A produced}}{\text{mole of B produced}} = \frac{\text{mole ratio of A half reaction}}{\text{mole ratio of B half reaction}}$$



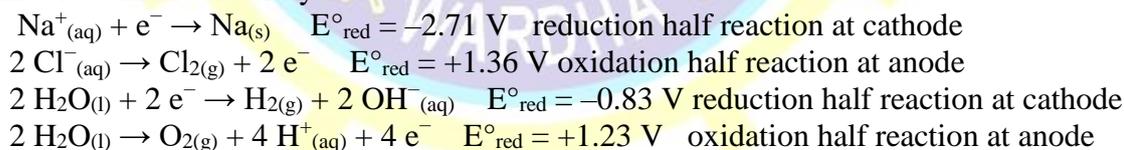
Electrolysis of molten sodium chloride NaCl

Fused NaCl Contains Na^+ and Cl^- ions When molten, the salt sodium chloride can be electrolyzed to give metallic sodium and gaseous chlorine. this process takes place in a special cell named Down's cell. The cell is connected to an electrical power supply, allowing electron to migrate from the power supply to the electrolyte Reactions that take place at Down's cell are the following

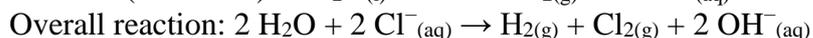
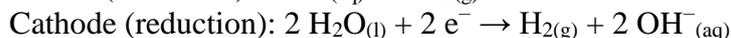


Electrolysis of aqueous NaCl solutions

An electrolysis of aqueous NaCl can be carried out using inert electrodes. Water is involved in the electrolysis NaCl

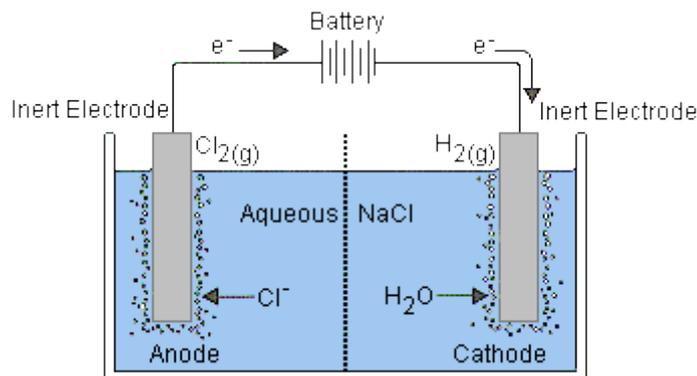


The overall reaction for the process according to the analysis would be the following



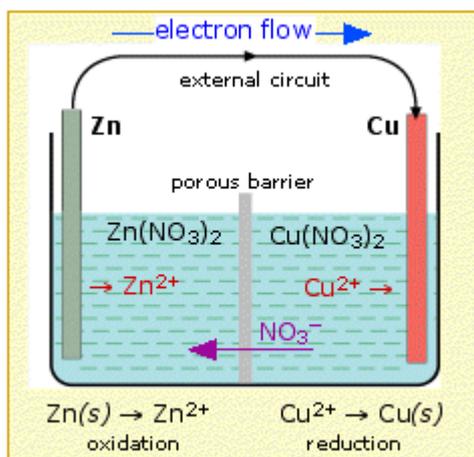
As the overall reaction indicates, the concentration of chloride ions is reduced in comparison to OH^- ions (whose concentration increases). The reaction also shows the production of gaseous hydrogen chlorine and aqueous sodium hydroxide.

The standard reduction potential for the reduction of water is higher than that for the reduction of Na^+ . this implies that water has much greater tendency to get reduced than Na^+ ion Hence, reduction of water is the cathode reaction for the electrolysis of aq. NaCl



4.5 Galvanic or voltaic cells

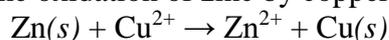
The names of cells, galvanic and voltaic are given in the honour of Italian scientists Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827) for their work in electrochemistry. It is physically impossible to measure the potential difference between a piece of metal and the solution in which it is immersed. We can, however, measure the *difference* between the potentials of two electrodes that dip into the same solution, or more usefully, are in two different solutions. In the latter case, each electrode-solution pair constitutes an oxidation-reduction *half cell*, and we are measuring the sum of the two *half-cell potentials*.



This arrangement is called a *galvanic cell*. A typical cell might consist of two pieces of metal, one zinc and the other copper, each immersed each in a solution containing a dissolved salt of the corresponding metal. The two solutions are separated by a porous barrier that prevents them from rapidly mixing but allows ions to diffuse through.

If we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain

when Zn^{2+} ions emerge from the zinc in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the oxidation of zinc by copper(II) ions:



but this time, the oxidation and reduction steps (half reactions) take place in separate locations:

Salt bridge

In galvanic cell, the solutions are connected by a salt bridge. It is an U shaped glass tube containing a saturated solution of an electrolyte such as KCl or NH_4NO_3 and 5% agar solution as shown in Fig. The ions of the electrolyte neither react with the ions of the electrode solutions neither oxidised nor reduced at the electrodes. The purpose of the salt bridge is to minimize the natural potential difference, known as the *junction potential*, that develops when any two are in contact. This potential difference would combine with the two half-cell potentials so as introduce a degree of uncertainty into

any measurement of the cell potential. With the salt bridge, we have two liquid junction potentials instead of one, but they tend to cancel each other out.

Functions of the salt bridge

- (i) It provides an electrical contact between the two solutions and thereby completes the electrical circuit .
- (ii) It prevents the mixing of electrode solutions.
- (iii) It maintain electrical neutrality in both the solutions by a flow of ions.

Representation or formulation of galvanic cells

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the cell we described above would be



- The *anode* is where oxidation occurs, and the *cathode* is the site of reduction. In an actual cell, the identity of the electrodes depends on the direction in which the net cell reaction is occurring.
- If electrons flow from the left electrode to the right electrode when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be positive.
- "Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

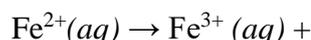
4.6 Types of electrodes

I) Redox electrodes

It consist of metal wire as an inert electrode immersed in a solution containing the ions of the same substance in two valency states

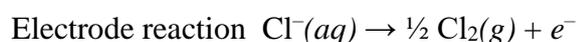
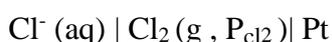


and the half-cell reaction would be



II) Gas electrodes

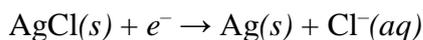
It consist of gas about an inert metal electrode immerse in a solution containing ion of the gas. For example – chlorine gas electrode



Similar reactions involving the oxidation of Br_2 or I_2 also take place at platinum surfaces.

III) Insoluble-salt electrodes

This type of electrode includes metal in contact with its sparingly soluble salt and aqueous solution of some salt containing same anion

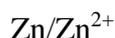


The half cell would be represented as



IV) Metal – Metal ion electrode

It consist of metal strip dipped in the solution of its own cations



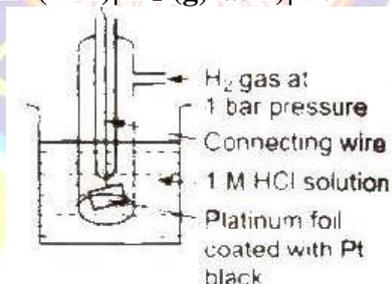
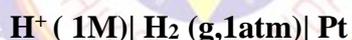
Reference Electrodes

i) Standard hydrogen Electrode- (SHE)

An electrode in which pure and dry hydrogen gas is bubbled at 1 atm pressure around a platinised platinum plate immersed in 1M H⁺ ion solution is called Standard hydrogen Electrode. It is primary reference electrode .

Standard hydrogen electrode 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 1M HCl. The hydrogen gas at 1 atm pressure is bubbled through the solution at 298K. Half-cell is consists of platinum wire, carrying platinum foil coated with finely divided platinum black.

The Standard hydrogen electrode Is represented as

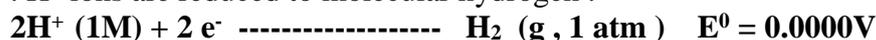


Electrode reaction

If the electrode is an anode in the galvanic cell , the half reaction occurring on it during the operation of the cell will be oxidation .hydrogen molecule will be oxidised to H⁺ ions



When the electrode serves as cathode in the galvanic cell the half reaction will be reduction . H⁺ ions are reduced to molecular hydrogen .



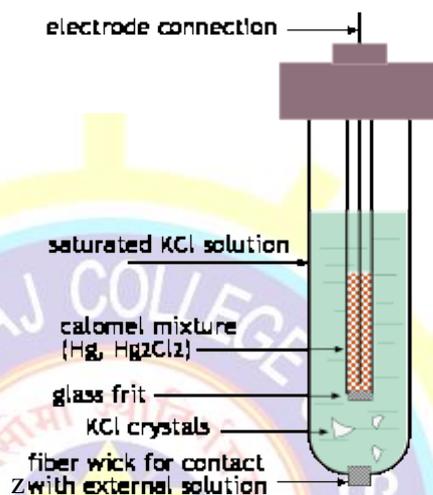
Its main drawbacks are

1. It is difficult to maintain 1 atm pressure of H₂ gas.
2. It is difficult to maintain H⁺ ion concentration 1 M.
3. The platinum electrode is easily poisoned by traces of impurities

Calomel electrode

It is metal sparingly soluble salt electrode. It is a secondary reference electrode

saturated calomel electrode



The electrode is represented as



Electrode Reactions

If the electrode is cathode (+) in the galvanic cell, the half reaction that occurs on it will be reduction



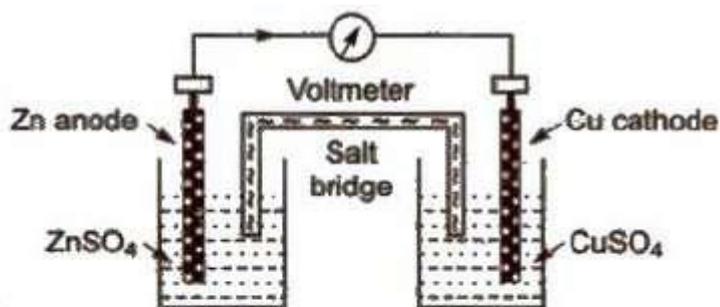
If it serves as anode (-) in the galvanic cell the half reaction will be oxidation



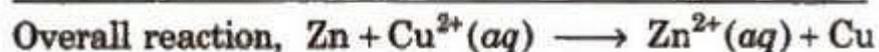
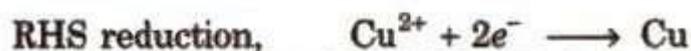
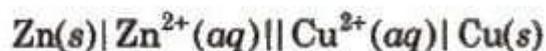
The potential of 0.1M, 1M and saturated calomel electrodes are 0.337V, 0.280V and 0.242V respectively.

4.7 Daniel Cell

It is a electrochemical cell in which spontaneous chemical reaction occurs to produce electricity.



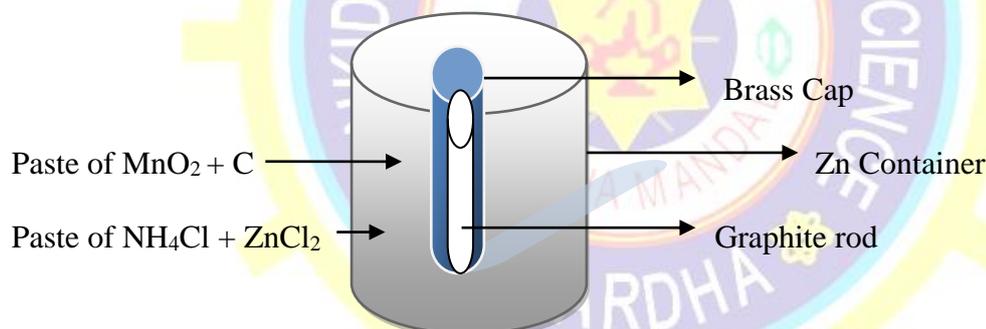
Cell diagram,



Emf of the cell is 1.1V

4.8 Dry cell (Leclanche cell)

It is a primary cell without liquid component but the electrolyte is completely dry.



Cell reaction

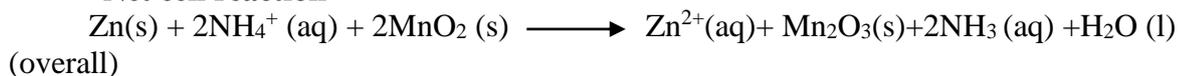
Oxidation at anode



Reduction at cathode



Net cell reaction

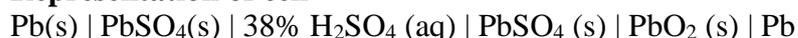


Lead accumulators (lead storage battery)

Construction

A group of lead plates pack with spongy lead serves as anode. Another group of lead plates with lead oxide as cathode. Two plates are alternately arranged. The electrodes are immersed in an aqueous solution of 38% of H₂SO₄ as an electrolyte.

Representation of cell

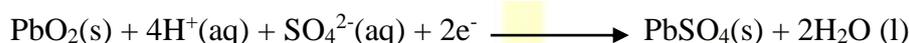


Electrode reaction during discharge

Oxidation at anode



Reduction at cathode



Net cell reaction



Emf of cell is around 2V

Electrode reaction during charging

Oxidation at anode



Reduction at cathode⁺



Net cell reaction



4.9 Hydrogen - oxygen fuel cell

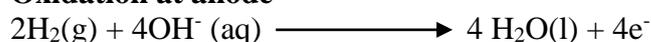
In hydrogen oxygen fuel cell the fuel used is hydrogen gas and oxygen gas is the oxidising agent. The energy of combustion of hydrogen is converted into electrical energy.

Construction

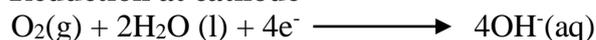
Anode consists of porous carbon rod containing finely divided platinum acting as a catalyst. H₂ gas is bubbled through anode and the cathode is porous carbon with finely divided platinum. O₂ gas is bubbled through cathode.

Cell reaction

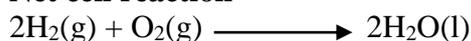
Oxidation at anode



Reduction at cathode



Net cell reaction



The cell potential is 1.23 V

4.10 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 corrosion.

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.

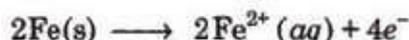
Anode- Pure iron

Cathode-Impure surface

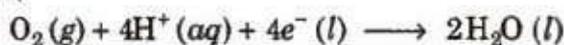
Electrolyte,



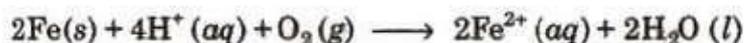
Anode reaction,



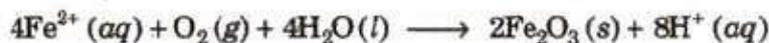
Cathode reaction,



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.

4.11 Electromotive Force (emf) of a Cell

It is the difference between the electrode potentials of two half-cells and cause flow of current from electrode at higher potential to electrode at lower potential. It is also the measure of free energy change. Standard emf of a cell,

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{oxi}}^{\circ}$$

Electrochemical Series

It is the arrangement of electrodes in the increasing order of their standard reduction potentials.

Standard Electrode Potential at 298K

Reaction (Oxidised form) + ne^{-}	→	Reduced form	E°/V
$F_2(g) + 2e^{-}$	→	$2F^{-}$	2.87
$Co^{3+} + e^{-}$	→	Co^{2+}	1.81
$H_2O_2 + 2H^{+} + 2e^{-}$	→	$2H_2O$	1.78
$MnO_4^{-} + 8H^{+} + 5e^{-}$	→	$Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + 3e^{-}$	→	$Au(s)$	1.40
$Cl_2(g) + 2e^{-}$	→	$2Cl^{-}$	1.36
$Cr_2O_7^{2-} + 14H^{+} + 6e^{-}$	→	$2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^{+} + 4e^{-}$	→	$2H_2O$	1.23
$MnO_2(s) + 4H^{+} + 2e^{-}$	→	$Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^{-}$	→	$2Br^{-}$	1.09
$NO_3^{-} + 4H^{+} + 3e^{-}$	→	$NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^{-}$	→	Hg_2^{2+}	0.92
$Ag^{+} + e^{-}$	→	$Ag(s)$	0.80
$Fe^{3+} + e^{-}$	→	Fe^{2+}	0.77
$O_2(g) + 2H^{+} + 2e^{-}$	→	H_2O_2	0.68
$I_2 + 2e^{-}$	→	$2I^{-}$	0.54
$Cu^{+} + e^{-}$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^{-}$	→	$Cu(s)$	0.34

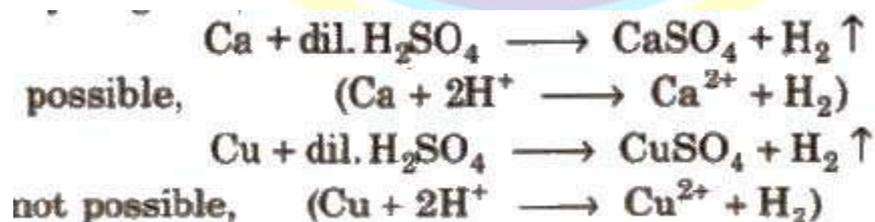
Reaction (Oxidised form) + ne	→	Reduced form	E° / V
AgCl(s) + e ⁻	→	Ag(s) + Cl ⁻	0.22
AgBr(s) + e ⁻	→	Ag(s) + Br ⁻	0.10
2H ⁺ + 2e ⁻	→	H ₂ (g)	0.00
Pb ²⁺ + 2e ⁻	→	Pb(s)	- 0.13
Sr ²⁺ + 2e ⁻	→	Sn(s)	- 0.14
Ni ²⁺ + 2e ⁻	→	Ni(s)	- 0.25
Fe ²⁺ + 2e ⁻	→	Fe(s)	- 0.44
Cr ³⁺ + 3e ⁻	→	Cr(s)	- 0.74
Zn ²⁺ + 2e ⁻	→	Zn(s)	- 0.76
2H ₂ O + 2e ⁻	→	H ₂ (g) + 2OH ⁻ (aq)	- 0.83
Al ³⁺ + 3e ⁻	→	Al(s)	- 1.66
Mg ²⁺ + 2e ⁻	→	Mg(s)	- 2.36
Na ⁺ + e ⁻	→	Na(s)	- 2.71
Ca ²⁺ + 2e ⁻	→	Ca(s)	- 2.87
K ⁺ + e ⁻	→	K(s)	- 2.93
Li ⁺ + e ⁻	→	Li(s)	- 3.05

Applications of Electrochemical Series (ECS)

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



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



3. Reducing character increases down the series.

4. Reactivity increases down the series.

5. Determination of emf; emf is the difference of reduction potentials of two half-cells. If the value of emf is positive, then reaction takes place spontaneously, otherwise not.

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

6. Greater the reduction potential of a substance, oxidising power. (e.g., F₂ > Cl₂ > Br₂ > I₂)

4.12 Nernst Equation

The Cell potential and electrode potential depends on temperature, concentration of solutes and partial pressure of gases. This dependence of potential is given by Nernst equation.

$$M^{n+} + ne^{-} \longrightarrow M$$

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

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{0.0591}{n} \log \left[\frac{1}{[M^{n+}]} \right]$$

For an electrochemical cell

$$aA + bB \longrightarrow cC + dD$$

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

Concentration of pure solid and liquid is taken as unity. Nernst equation and K_c at equilibrium

$$\therefore \text{At equilibrium, } E_{\text{cell}} = 0$$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c \text{ at } 298\text{K}$$

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

Here, ΔG° is the standard Gibbs free energy change.

Type of reaction	ΔG°	E_{cell}°	Type of cell
Spontaneous	-ve	+ve	Galvanic
Non-spontaneous	+ve	-ve	Electrolytic
Equilibrium	0	0	Dead battery

Standard cell potential and equilibrium constant

Relationship between free energy change and equilibrium constant

$$1) \Delta G^{\circ} = -2.303RT \log K_c$$

Relation between standard Gibbs free energy change of the cell and emf of the cell is given by the equation

$$2) \Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

From equation 1 and 2

$$E^0_{\text{cell}} = \frac{0.0592}{n} \log_{10}K$$

