

Electrochemistry

Class
12

Revision Notes

CHEMISTRY

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7404044544

Part – 1

1.1 Introduction

Electrochemistry is a branch of chemistry which deals with the relationship between chemical change and electrical energy taking place in redox reactions.

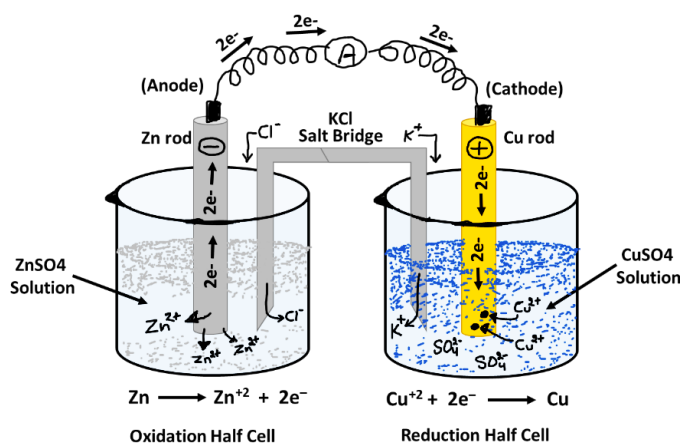
The three main aspects of study in the branch of Electrochemistry are :

1.) Electrochemical Cells 2.) Electrolytic conduction 3.) Electrolysis

1.2 Electrochemical Cell or Galvanic Cell

A device used to convert the chemical energy of a spontaneous redox reaction into electrical energy is called an electrochemical cell.

1.2.1 Construction of Electrochemical Cell



Take two beakers and filled them with **1M ZnSO₄** solution and **1M CuSO₄** solution separately. Put **Zn rod** in **ZnSO₄** solution and put **Cu rod** in **CuSO₄** solution. Now, connect the both Zn rod and Cu rod by a copper wire through **voltmeter or ammeter**. Also connect the solutions in the two beakers by a **salt bridge** which provides electrical contact without allowing them to mix with each other.

Left Beaker: Zinc rod starts dissolving due to oxidation of metallic Zn into Zn⁺² ion and release two electrons. As a result of more Zn⁺² ions in solution, the ZnSO₄ solution becomes more concentrated. The released two electrons move through the wire toward copper electrode.

The chemical reaction takes place in left beaker is:

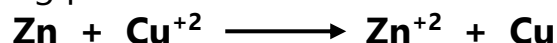


Right Beaker: The electrons released by Zn rod reach to the Cu rod where these electrons are gained by **Cu⁺²** ions present in solution. By gaining electrons Cu⁺² ions reduced into metallic Cu which starts deposit on Cu rod and hence, the CuSO₄ solution starts getting diluted.

The chemical reaction takes place in right beaker is:



Overall reaction taking place in two beakers is:



Note:

The solutions present in these two beakers are connected by salt bridge.

Salt Bridge:

It is inverted U-shaped glass tube containing saturated solution of inert electrolyte (i.e., KCl, K₂SO₄, KNO₃, NH₄NO₃ etc.) in agar-agar or gelatine.

Functions of Salt Bridge:

- It allows the movement of ions from one solution to other without mixing of the two solutions.
- It helps to maintain the electrical neutrality of the solutions in two half cells.
- It completes the electrical circuit of the cell.

1.2.2 Salient feature of an Electrochemical Cell

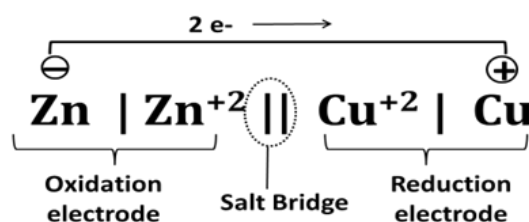
- Oxidation occurs at the anode while reduction occurs at the cathode.
- Anode acts as a negative pole while Cathode act as positive pole.
- Electrons flows from anode to cathode while current flows from cathode to anode.
- The two-half reactions always take place simultaneously.
- The weight of cathode rod will increase while that of anode rod will decrease as the cell works.
- A salt bridge completes the inner electrical circuit of the cell and maintains the electrical neutrality of the electrolytes in the two half cells.

1.2.3 Representation of an Electrochemical Cell

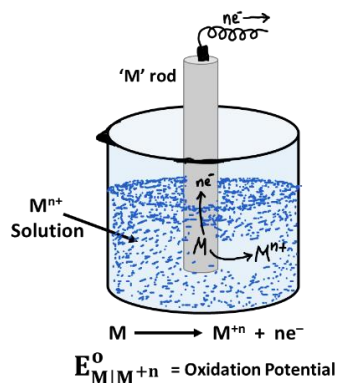
- The electrode on which oxidation occurs written on **left** hand side.
- The electrode on which reduction occurs written on **right** hand side.
- The left electrode is written in such a way that symbol of metal is written first followed by the symbol of ion.
- The right electrode is written in such a way that symbol of ion is written first followed by the symbol of metal.
- Single vertical lines represent the **interface** between the two phases.
- The double-parallel line represents the **salt-bridge**.

Example :

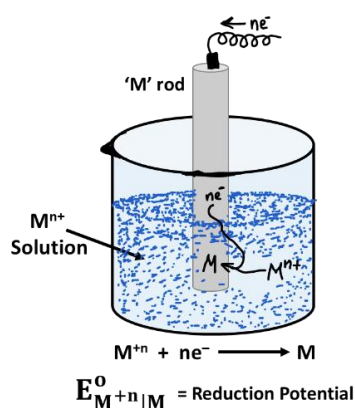
- $\text{Zn} | \text{Zn}^{+2} || \text{Cu}^{+2} | \text{Cu}$
- $\text{Cu} | \text{Cu}^{+2} || \text{Ag}^+ | \text{Ag}$
- $\text{Zn} | \text{Zn}^{+2} || \text{Ag}^+ | \text{Ag}$
- $\text{Fe} | \text{Fe}^{+2} || \text{Cu}^{+2} | \text{Cu}$
- $\text{Fe} | \text{Fe}^{+2} || \text{Ag}^+ | \text{Ag}$

**1.3 Standard Electrode Potential**

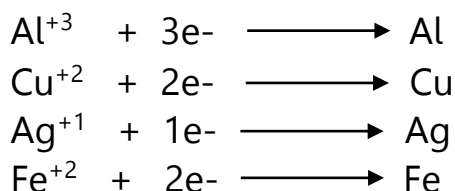
It can be defined as the tendency of an electrode to lose or gain electrons, when the rod is dipped in its own ionic solution whose concentration is 1M. It is denoted by E° . An electrode potential is of two types

1.3.1 Oxidation Electrode Potential

The tendency of an electrode to lose electrons, when the rod is dipped in its own ionic solution whose concentration is 1M.

**1.3.2 Reduction Electrode Potential**

The tendency of an electrode to gain electrons, when the rod is dipped in its own ionic solution whose concentration is 1M.

**Factors Affecting Electrode Potential:**

- The nature of metal and its ions.
- The concentration of the ions in its solution.
- Temperature.

Therefore, standard electrode potentials are generally measured under standard conditions such as 1M ionic concentration and a temperature of 298K.

Note:

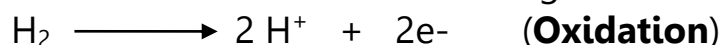
Oxidation potential and reduction potential are reverse of each other. They have the same value but opposite signs. **+RP = -OP** OR **-RP = +OP**
For example: The standard reduction potential of silver is +0.80 volt. Its standard oxidation potential will be -0.80 volt.

1.4 Measurement of Standard Electrode Potential

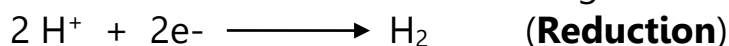
The standard electrode potentials of different elements must be measured against standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE).

Standard Hydrogen Electrode (SHE) consists of platinized platinum electrode dipped in 1M solution of H^+ ions (1M HCl) at 298 K and pure hydrogen gas maintained at a pressure of 1 atm is bubbled through the solution containing platinum electrode. The electrode potential of SHE is taken as **zero** (0.00 V).

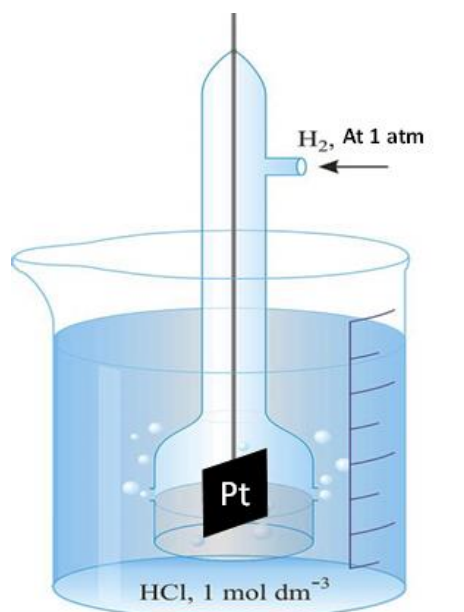
When SHE acts as anode, the following reaction occurs:



When SHE acts as cathode, the following reaction occurs:



SHE is usually represented as : $E^{\circ}_{H^+|H_2,Pt} = 0.00 \text{ V}$

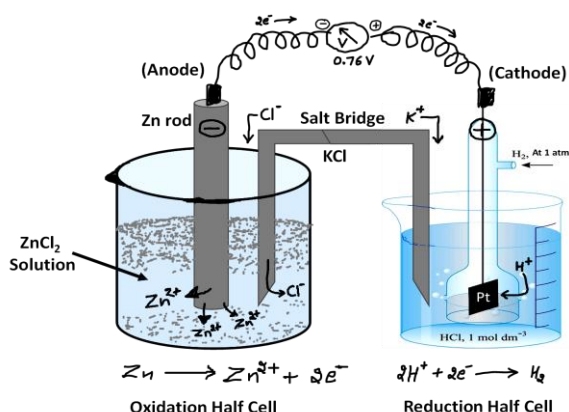




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1.4.1 Determination of standard electrode potential of Zn electrode



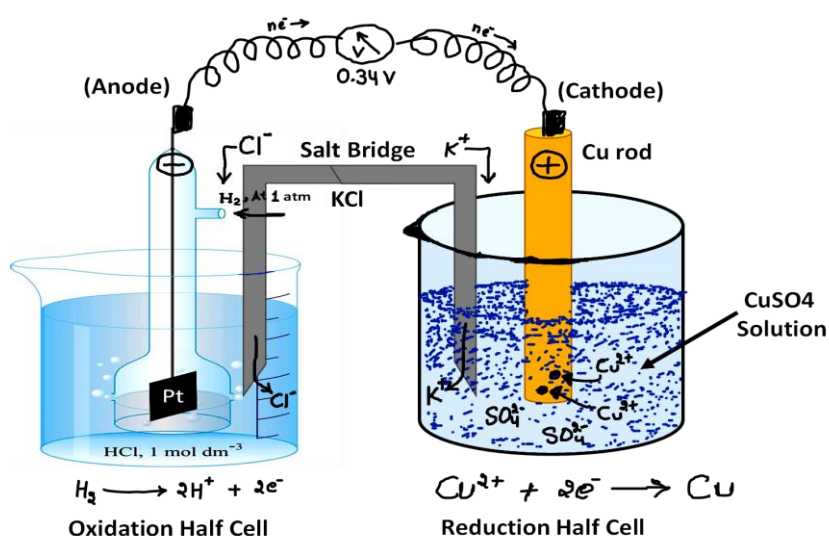
An electrochemical cell is setup by using one electrode of Zinc immersed in 1M ZnCl_2 solution and second electrode of S.H.E. The EMF of the above cell comes out to be 0.76 V. Further, the direction of flow of current indicates that oxidation takes place at the zinc electrode. Hence 0.76 V is the standard oxidation potential of the Zinc electrode.

It is important to mention here that it is common practice to express all the electrode potentials as **reduction potentials**. ($\text{OP} = -\text{RP}$)

Thus, for the Zinc electrode, Standard Reduction Potential is **-0.76 V**

1.4.2 Determination of standard electrode potential of Cu electrode

An electrochemical cell is setup by using one electrode of copper immersed in 1M CuSO_4 solution and second electrode of S.H.E. The EMF of the above cell comes out to be 0.34 V. Further, the direction of flow of current indicates that reduction takes place at the Copper electrode. Hence, +0.34V is the standard reduction potential of the Copper electrode.



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1.5 Electrochemical Series or Electromotive Series

The standard electrode potentials of number of electrodes at 1M ionic concentration at 298 K are arranged in series in such a way that as we move down the series (positive potential value to negative potential value) their reducing agent character increase and oxidising agent character decreases.

	Reaction (Oxidised form + ne ⁻ → Reduced form)	E ⁰ /V
↑ Increasing strength of oxidising agent	F ₂ (g) + 2e ⁻ → 2F ⁻	2.87
	Co ³⁺ + e ⁻ → Co ²⁺	1.81
	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O	1.78
	MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	1.51
	Au ³⁺ + 3e ⁻ → Au(s)	1.40
	Cl ₂ (g) + 2e ⁻ → 2Cl ⁻	1.36
	Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻ → 2Cr ³⁺ + 7H ₂ O	1.33
	O ₂ (g) + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.23
	MnO ₂ (s) + 4H ⁺ + 2e ⁻ → Mn ²⁺ + 2H ₂ O	1.23
	Br ₂ + 2e ⁻ → 2Br ⁻	1.09
	NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO(g) + 2H ₂ O	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 ₂ O ₂	0.68
	I ₂ + 2e ⁻ → 2I ⁻	0.54
	Cu ⁺ + e ⁻ → Cu(s)	0.52
	Cu ²⁺ + 2e ⁻ → Cu(s)	0.34
	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
	Sn 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	

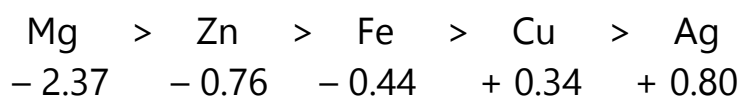
1.6 Applications of the Electrochemical Series

1.6.1 To compare the relative oxidizing and reducing power.

As we know that all the electrode potentials in an electrochemical series are reduction potentials. It means that greater the value of E.P. in the series, more easily is the substance reduced, hence, behaves as a strong oxidizing agent.

1.6.2 To compare the relative activities of metals.

The reactivity of a metal increases with decrease in the value of electrode potential in electrochemical series.



1.6.3 To predict whether a metal reacts with acid to give H₂ gas.

Acids have H⁺ ions, which gain electrons from metal atoms and liberate H₂ gas. It means, any metal with low reduction potential (i.e., high oxidation potential) can react with acids and liberate hydrogen gas. Hence, metal with –ve reduction potential can react with acids such as Mg, Fe, Zn etc. but metals with +ve reduction potential do not react with acids such as Cu, Ag, Au etc.

1.6.4 To predict the spontaneity of a redox reaction.

For a spontaneous redox reaction, the EMF of the cell must be positive. If the EMF comes out to be negative, the direct reaction cannot take place, however, reverse reaction may take place.

1.6.5 To calculate the standard EMF of any electrochemical cell.

The difference between reduction electrode potentials of the two half cells in an electrochemical cell is known as **cell potential** or **cell voltage**.

It may be called **electromotive force** (or **EMF**) of the cell if no current is drawn from the cell.

Hence,

$$\text{Standard EMF of the cell } (E_{\text{cell}}^0) = \left(\begin{array}{c} \text{Standard} \\ \text{Reduction} \\ \text{Potential of the} \\ \text{Reduction half cell} \end{array} \right) - \left(\begin{array}{c} \text{Standard} \\ \text{Reduction} \\ \text{Potential of the} \\ \text{Oxidation half cell} \end{array} \right)$$

: In Short :

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Red Half cell}}^0 - E_{\text{Oxi Half Cell}}^0 \\ &= E_{\text{Cathode}}^0 - E_{\text{Anode}}^0 \end{aligned}$$

: Note :

$$E_{\text{cell}}^0 = \text{Reduction Potential} + \text{Oxidation Potential}$$

As we know:

$$\text{Oxidation Potential} = - \text{Reduction Potential}$$

$$E_{\text{cell}}^0 = \text{Red Potential}(\text{red half cell}) - \text{Red Potential}(\text{oxi half cell})$$

Difference between EMF and Potential difference**i. EMF (Electromotive Force)**

- EMF is the potential difference between the two electrodes of the cell when no current is flowing in the circuit (i.e., in an open circuit).
- EMF can be measured by potentiometric method.
- EMF is the maximum voltage obtain from the cell.
- The magnitude of EMF has always remained constant.
- EMF does not depend on the internal resistance of the circuit.

ii. Potential Difference

- Potential difference is the difference between electrode potentials of the two electrodes under any condition (i.e., in a close circuit).
- It can be measured by a simple voltmeter.
- It is less than the maximum voltage obtained from the cell.
- The magnitude of potential difference varies.
- Potential difference depends on the internal resistance of the circuit. It is directly proportional to the resistance of the circuit.



1.7 Effect of Electrolyte Concentration and Temperature on Electrode Potential (NERNST Equation)

The mathematical relationship between electrode potential and concentration of solution at a particular temperature is given by NERNST equation.

Consider a hypothetical reduction-half reaction : $M^{n+} + ne^{-} \longrightarrow M$

Then the Nernst equation is applied to above reduction-half reaction :

$$E_{M^{n+}|M} = E_{M^{n+}|M}^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$\ln x = 2.303 \log x$$

Where:

$E_{M^{n+}|M}$ is electrode potential under a particular conc. and temp.

$E_{M^{n+}|M}^0$ is standard electrode potential when conc. is 1M and temp. is 298 K.

'n' is number of electron exchange in the electrode reaction

'R' is gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

'T' is temperature in Kelvin

'F' is Faraday electricity ($1F = 96500 \text{ C}$) (Charge on 1 mole electrons)

$$E_{M^{n+}|M} = E_{M^{n+}|M}^0 - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}|M} = E_{M^{n+}|M}^0 - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M]}{[M^{n+}]} \quad \text{at } 25^\circ\text{C}$$

$$E_{M^{n+}|M} = E_{M^{n+}|M}^0 - \frac{0.0591}{n} \log \frac{[M]}{[M^{n+}]} \quad \text{at } 25^\circ\text{C}$$

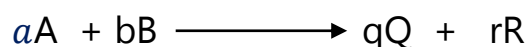
For pure solids or liquids or gases at 1 atm pressure, the molar concentration is taking as unity. For example: $[M]$ or $[Zn]$ or $[Cu]$ or $[Br_2]$ or $[H_2] = 1$

$$E_{M^{n+}|M} = E_{M^{n+}|M}^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad \text{at } 25^\circ\text{C}$$

Note: While applying NERNST equation, electrode potential is always taken as reduction potential.

1.7.1 NERNST Equation for Electrochemical Cell

In general, if the cell reaction is



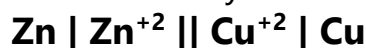
Then applying NERNST equation, we have :

$$E_{\text{cell}} = E_{\text{Cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[Q]^q [R]^r}{[A]^a [B]^b}$$

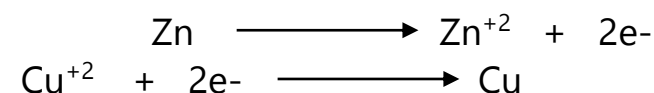
$$E_{\text{cell}} = E_{\text{Cell}}^0 - \frac{0.0591}{n} \log \frac{[Q]^q [R]^r}{[A]^a [B]^b} \quad \text{at } 25^\circ\text{C}$$

1.8 Equilibrium Constant (K_c) from NERNST Equation

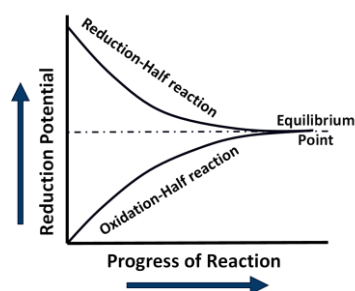
Consider an electrochemical cell formed by combination of zinc electrode and copper electrode :



The chemical reaction takes place in the cell will be :

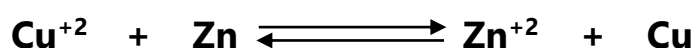


From above equation we conclude that as the reaction proceed, the concentration of copper ions decreases whereas that of zinc ion increases.



Electrode potential of zinc electrode will keep on increasing while that of copper electrode will keep on decreasing. Ultimately, a stage comes when the electrode potentials of the zinc and copper becomes equal and the current stops flowing in the circuit, this means **EMF of the cell becomes Zero**.

At this stage the concentration of zinc ion and copper ion are equilibrium concentrations and their ratio product will give equilibrium constant (K_c).



$$\frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]} = K_c$$

Applying NERNST equation :

$$E_{\text{cell}} = E_{\text{Cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[\text{Zn}^{+2}]}{[\text{Cu}^{+2}]}$$

As we know that at equilibrium $E_{\text{cell}} = 0$

Hence,

$$0 = E_{\text{Cell}}^0 - \frac{2.303 RT}{nF} \log K_C \quad \text{OR} \quad E_{\text{Cell}}^0 = \frac{2.303 RT}{nF} \log K_C$$

At 25 °C or 298 K

$$E_{\text{Cell}}^0 = \frac{0.0591}{n} \log K_C \quad \text{OR} \quad \log K_C = \frac{n E_{\text{Cell}}^0}{0.0591}$$

1.8.1 Significance of Equilibrium Constant (K_C)

The value of K_C gives the extent to which a cell reaction proceeds. Larger the value of K_C , larger is the extent to which the cell reaction proceeds. The magnitude of K_C can give us some information about the reactant and product concentrations at equilibrium.

For example,

- If K_C is larger than 1000, we will have mostly product present at equilibrium.
- If K_C is lower than 0.001, we will have mostly reactant present at equilibrium.
- If K_C is between 0.001 and 1000, we will have significant concentration of both reactant and product at equilibrium.

1.9 Gibb's Free Energy and Cell Potential

In an electrochemical cell, the free energy present in the system is converted to electrical energy. Therefore, electrical work done by a cell results in decrease in the free energy of the system.

Hence, $\Delta G = W_{\text{electrical}} = -n F E_{\text{Cell}} \quad \text{OR} \quad -\Delta G = n F E_{\text{Cell}}$

Where, ' n ' is number of moles of electrons transferred in reaction of the cell, And, ' F ' is the Faraday's constant (the charge on one mole of electrons) ($1F = 96500 \text{ C}$).

As standard cell potentials (E_{cell}^0) are used to compare different cells. The free energy change is called standard free energy ($\Delta^\circ G$)

$$\Delta^\circ G = -n F E_{\text{cell}}^0 \quad \text{OR} \quad -\Delta^\circ G = n F E_{\text{cell}}^0$$

As we know : $E_{\text{Cell}}^0 = \frac{2.303 RT}{nF} \log K_C$

Hence, $\Delta^\circ G = -nF \frac{2.303 RT}{nF} \log K_C = -2.303 RT \log K_C$

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

Exercises

- How would you determine the standard electrode potential of the system $Mg^{+2}|Mg$?
- Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.
- Represent the cell in which the following reaction takes place
 $Mg_{(s)} + 2Ag^+_{(0.0001 M)} \rightarrow Mg^{+2}_{(0.130 M)} + 2Ag_{(s)}$
 Calculate its E_{cell} if $E^\circ_{cell} = 3.17 V$
- Calculate the equilibrium constant of the reaction: (Given $E^\circ_{cell} = 0.46 V$)
 $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{+2}_{(aq)} + 2Ag_{(s)}$
- Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.
- Calculate the emf of the cell in which the following reaction takes place:
 $Ni_{(s)} + 2Ag^+_{(0.002 M)} \rightarrow Ni^{+2}_{(0.160 M)} + 2Ag_{(s)}$ Given that $E^\circ_{cell} = 1.05 V$
- The cell in which the following reaction occurs:
 $2Fe^{+3}_{(aq)} + 2I^-_{(aq)} \rightarrow 2Fe^{+2}_{(aq)} + I_{2(s)}$ has $E^\circ_{cell} = 0.236 V$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.



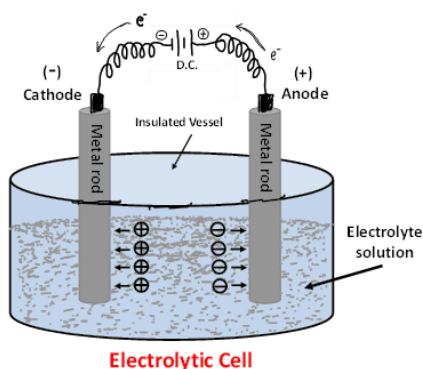
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Part – 2

2.1 Electrolytic Cell and Electrolysis



Electrolytic cell is a device or apparatus which is used to bring about electrolysis. In other words, electrolytic cell is a device which converts electric energy into chemical energy.

It consists of an insulated vessel in which molten or aqueous solution of electrolyte is taken. Two chemically inert metal rods are dipped into it and are connected to the D.C. electric source.

Electrolysis is a process of decomposition of an electrolyte by the passage of electricity through its molten or aqueous state. In electrolysis a non-spontaneous redox reaction is forced to occur with the help of electrical energy.

2.1.1 Mechanism of electrolysis

It can be easily explained based on **ionization theory**. According to this theory, when an electrolyte is taken in molten or aqueous state, it dissociates to produce negatively and positively charged ions. These ions start move towards oppositely charged electrodes when electric current is applied. Cations move towards cathode (negative electrode) while anions move towards anode (positive electrode). Here, these ions loss or gain the electrons and become neutral species, this process is called **primary change**. The product formed as a result of primary change may be collected as such or it may undergo a **secondary change** to form the final product.

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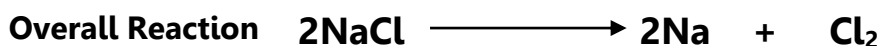
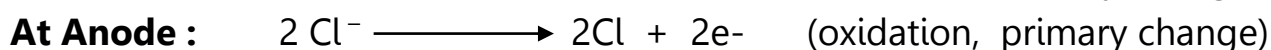
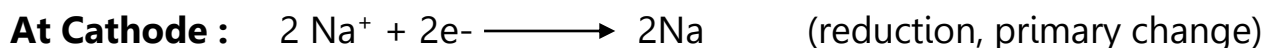
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Example: Electrolysis of molten NaCl

On passing electricity, Na^+ ions move toward cathode while Cl^- ions move towards anode. Na^+ ions gain electrons and start depositing at cathode while Cl^- ions lose electrons and become neutral chlorine atoms. Since chlorine atoms are unstable, they undergo secondary change to form Cl_2 gas molecules and start liberating at the anode.

**2.1.2 Difference between Electrochemical cell and Electrolytic cell**

Electrochemical Cell	Electrolytic Cell
<ul style="list-style-type: none"> It is a device which converts chemical energy into electrical energy The redox reaction is of spontaneous nature. The two electrodes are dipped in different electrolytes taken in different beakers. Anode is negative while cathode is positive. Both the electrodes are of different materials. A salt bridge or porous pot is used to separate the two half cells. 	<ul style="list-style-type: none"> It is a device which converts electrical energy into chemical energy The redox reaction is of non-spontaneous nature. Both the electrodes are placed in the solution or molten electrolyte in the same beaker. Anode is positive while cathode is negative. The electrodes may be of the same or different materials. No salt bridge or porous pot is needed in this case.



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2.2 Quantitative Aspects of Electrolysis and Faraday's Law

2.2.1 Faraday's First Law of Electrolysis

According to this law, the amount of substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the molten or aqueous solution of electrolyte.

$$w \propto Q \quad \text{OR} \quad w = Z Q$$

Where, w = weight of substance deposited or liberated in grams

Q = Quantity of electricity in coulombs

Z = Proportionality constant or electrochemical equivalent constant

As we Know, $Q = I \times t$ Then, $w = Z \times I \times t$

If, 1 ampere current is passed for 1 sec or 1 coulombs of electricity is passed, then, $w = Z$ $I = 1$ ampere , $t = 1$ sec

"Z" Electrochemical equivalent constant of a substance may be defined as the mass of substance deposited or liberated at any electrode when 1 ampere current is passed for 1 sec (or 1 Coulombs of electricity is passed).

Note:

Equivalent weight of a substance = $Z \times 1F = Z \times 96500$

(Equivalent weight of a substance may be defined as the mass of substance deposited or liberated at any electrode when 1F or 96500 Coulombs of electricity is passed).

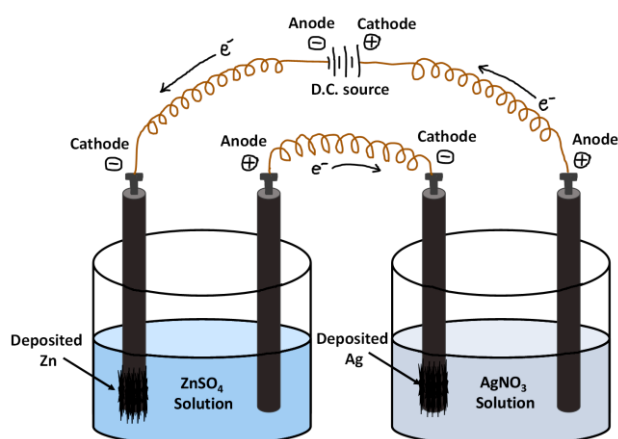
Atomic Mass of a substance = Equivalent weight \times n-factor



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2.2.2 Faraday's Second Law of Electrolysis



According to this law, when the same quantity of electricity is passed through the solutions of different electrolytes connected in series, the mass of substances deposited on electrodes are directly proportional to their equivalent weights.

For example:

When ZnSO₄ solution and AgNO₃ solution are connected in series and same quantity of electricity is passed through them, then

$$\frac{\text{Mass of Ag deposited}}{\text{Mass of Zn deposited}} = \frac{\text{Equivalent weight of Ag}}{\text{Equivalent weight of Zn}}$$

This law can also be derived from first law as follows :

According to Faraday's first law of electrolysis : $w = Z \times Q$

If same quantity of electricity is passed through solution of both electrolytes, then,

$$Q_1 = Q_2 = Q$$

In case of first electrolyte : $w_1 = Z_1 \times Q$

In case of second electrolyte : $w_2 = Z_2 \times Q$

On dividing, $\frac{w_1}{w_2} = \frac{Z_1 \times Q}{Z_2 \times Q} = \frac{Z_1}{Z_2}$ As we know : $Z = \frac{\text{Equivalent weight}}{96500} = \frac{E}{96500}$

Thus,

$$\frac{w_1}{w_2} = \frac{Z_1}{Z_2} = \frac{E_1 / 96500}{E_2 / 96500} = \frac{E_1}{E_2}$$

2.2.3 Quantitative Aspects from Faraday's laws of Electrolysis

By taking example of some half reactions such as:



We conclude that, **1 mole** of electrons are required to deposit 1 mole of Na whereas **2 moles** of electrons are required to deposit 1 mole of copper.

We know that 1 mole of any element is equal to the gram atomic mass of that element. It means that number of moles of electron require to deposit 1 mole of any element is just multiple of the charge carried by that element in ionic state.

The charge carried by 1 mole of electrons can be obtained by multiplying the charge present on 1 electron with Avogadro's number.

$$\begin{aligned}\text{Charge of 1 mole electron} &= (1.6 \times 10^{-19} \text{ C}) \times (6.022 \times 10^{23}) \\ &= 96487 \text{ C/mol} \quad \text{OR} \quad 96500 \text{ C/mol} \quad \text{OR} \quad 1\text{F}\end{aligned}$$

In term of gram equivalent weight, it may be remembered that One Faraday (1F or 96500 C) of electricity deposits one gram equivalent of the substance. Hence,

$$\text{Equivalent weight of any element} = \frac{\text{Atomic Weight of the element}}{\text{No. of electrons gained or lost by element}}$$

Another two important conclusions are,

$$\text{Equivalent weight of substance} = \frac{\text{Weight deposited on electrode} \times 96500}{\text{Quantity of electricity passed}}$$

$$\text{Electrochemical equivalent constant (Z)} = \frac{\text{Equivalent weight of the substance}}{96500}$$

2.3 Products of Electrolysis

The products of electrolysis depend upon several factors, such as:

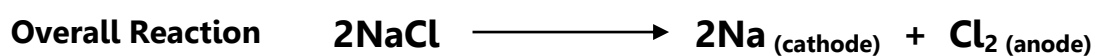
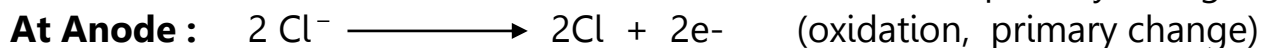
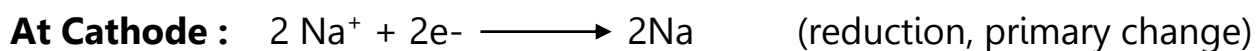
- Nature of Electrolyte
- Types of Electrodes
- Oxidising and reducing species present in electrolytic cell and their standard electrode potentials.

There are two types of electrodes, attackable and non-attackable. The non-attackable electrodes are also called inert electrodes (i.e., Platinum or Gold). They simply act as carriers for the electrons. While the attackable electrodes (i.e., Copper or Carbon) takes part in the chemical reactions and influence the nature of the products.

2.3.1 Electrolysis of molten NaCl



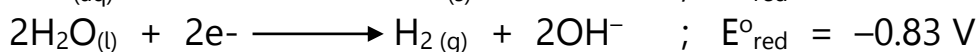
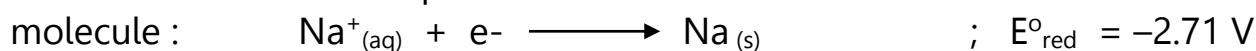
On passing electricity, Na^+ ions move toward cathode while Cl^- ions move towards anode. Na^+ ions gain electrons and start depositing at cathode while Cl^- ions lose electrons and become neutral chlorine atoms. Since chlorine atoms are unstable, they undergo secondary change to form Cl_2 gas molecules and start liberating at the anode.



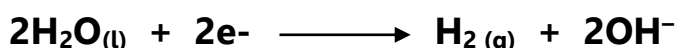
2.3.2 Electrolysis of Aqueous NaCl



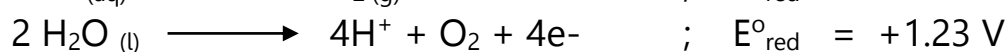
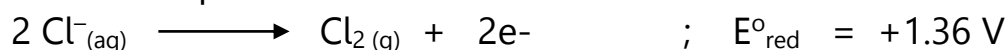
At Cathode there is competition for reduction between Na^+ and H_2O



Here, the reaction with higher reduction potential value is preferred, so it is much easier to reduce H_2O than Na^+ ion. Hence, Hydrogen gas will liberate at cathode.

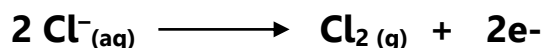


At Anode there is competition for oxidation between Cl^- and H_2O molecule :

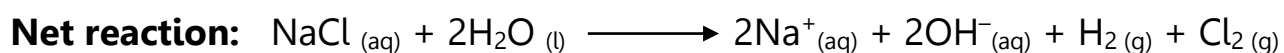
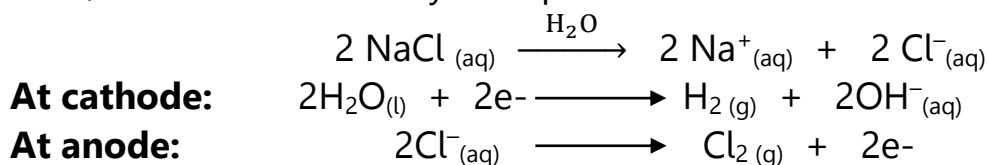


Here, the reaction with lower reduction potential value is preferred, the standard reduction potential of H_2O and Cl^- are almost equal and therefore, they have equal chances of being oxidised under similar conditions and we might expect the mixture of O_2 and Cl_2 gas collect at the anode.

But in practice, Cl_2 gas collects at anode. This is due to the **overpotential** of oxygen (means reaction require extra voltage to occur). The pH of the electrolytic cell keeps on increasing with the reaction, which increases the reduction potential of H_2O . Under ideal conditions, 1.23 V potential is sufficient to oxidise H_2O to O_2 gas. In real conditions, however, it may take a very high voltage to initiate this reaction. (The overvoltage for H_2O oxidation can be as large as 1 V). Hence, Chlorine gas will liberate at anode.



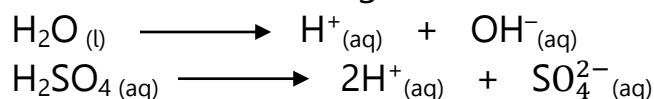
Thus, the net reaction may be represented as :



Thus, we may sum up that during electrolysis of aqueous NaCl, Hydrogen gas is evolved at cathode and Chlorine gas is evolved at anode. The solution contains both Na^+ ions and OH^- ions. The electrolysis of aqueous NaCl is called **Chlor-alkali process**.

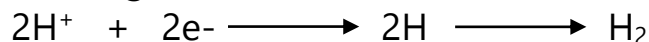
2.3.3 Electrolysis of Acidulated Water (or dilute H_2SO_4)

Pure water is poor conductor of electricity because it is weakly ionised. However, acidulated water becomes a good conductor.

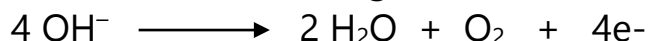


There are three ions in water acidulated with sulphuric acid ; H^+ , OH^- , SO_4^{2-}

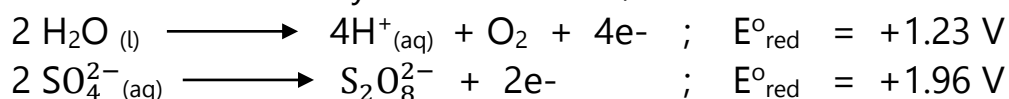
At Cathode : H^+ ions migrate towards cathode and liberate H_2 gas by gaining electrons.



At Anode : Both OH^- and SO_4^{2-} ions migrate towards anode.



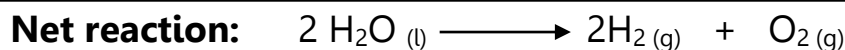
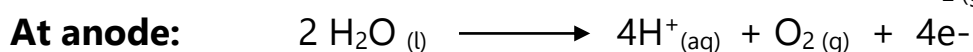
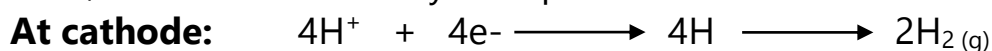
but OH^- ions are formed by H_2O molecules, so



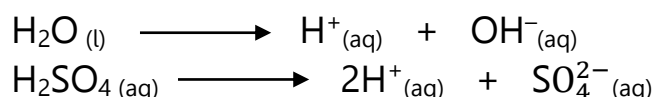
Reaction with lower reduction potential value is preferred, SO_4^{2-} ions remain in solution.



Thus, the net reaction may be represented as :

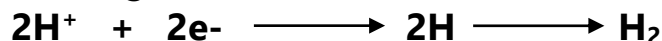


2.3.4 Electrolysis of Concentrated H₂SO₄

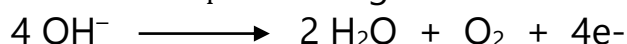


There are three ions in concentrated sulphuric acid ; H⁺ , OH⁻ , SO₄²⁻

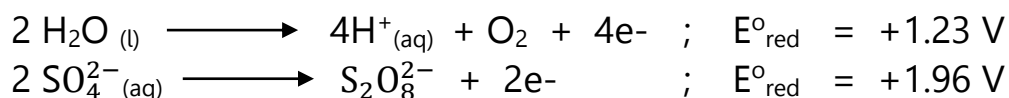
At Cathode : H⁺ ions migrate towards cathode and liberate H₂ gas by gaining electrons.



At Anode : Both OH⁻ and SO₄²⁻ ions migrate towards anode.

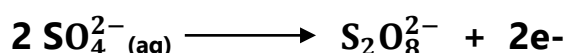


but OH⁻ ions are formed by H₂O molecules, so

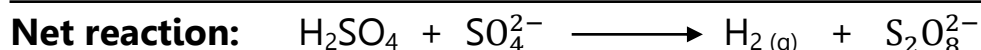
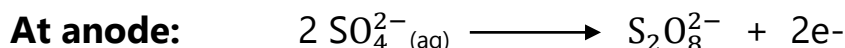
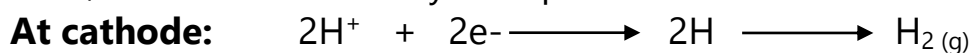


Reaction with lower reduction potential value is preferred, but due low pH and high conc. of SO₄²⁻ ions the **overpotential** of oxygen comes into act.

Hence, oxidation of SO₄²⁻ ions will take place at anode.



Thus, the net reaction may be represented as :



Or



H₂S₂O₈ is Peroxydisulphuric acid. Also called **Marshall's acid** after its inventor Professor Hugh Marshall.



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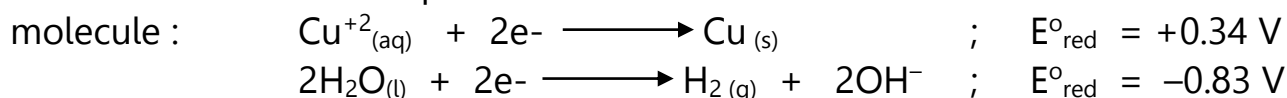
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2.3.5 Electrolysis of Aqueous CuSO_4 (Using inert electrodes, i.e., Pt)



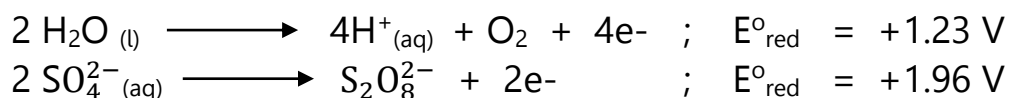
At Cathode there is competition for reduction between Cu^{2+} and H_2O



Here, the reaction with higher reduction potential value is preferred, so it is much easier to reduce $\text{Cu}^{2+}(\text{aq})$ ion. Hence, Copper will deposit at cathode.



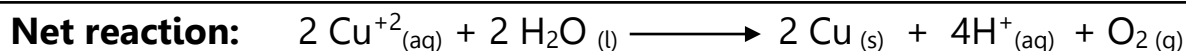
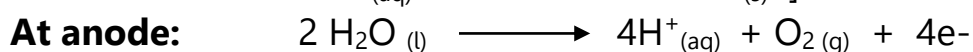
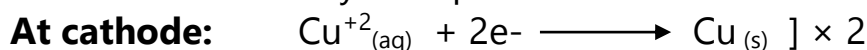
At Anode : Both H_2O and SO_4^{2-} ions migrate towards anode for oxidation.



Reaction with lower reduction potential value is preferred, SO_4^{2-} ions remain in solution.



The net reaction may be represented as :



Thus, as a result of electrolysis, copper is deposited on the cathode while oxygen is liberated at the anode. The solution contains H_2SO_4 and is, therefore, acidic in nature.

2.4 Electrolytic Conduction

The movement of the ions of the electrolyte towards the oppositely charged electrodes under the influence of electric field is called electrolytic conduction.

2.4.1 Strong and Weak Electrolytes

- **Strong electrolytes** are those substances which are completely dissociated or ionised in their aqueous solution. Their solution exhibit high electrical conductivity. Example: NaCl , KCl , CuSO_4 , HCl , HNO_3 , H_2SO_4 , KOH , NaOH etc.
- **Weak electrolytes** are those substances which are dissociated into ions only to a small extent in their aqueous solution. Their solution exhibit low electrical conductivity. Their extent of dissociation is indicated by degree of dissociation (α). Example: CH_3COOH , $\text{C}_6\text{H}_5\text{COOH}$, NH_4OH etc.

2.4.2 Factors Affecting Electrical Conductivity of Solution

- **Viscosity of Solvent (solvent-solvent interaction)**

Electrolytic conductance decreases with increase in viscosity of the solution. Larger the solvent-solvent interaction, larger will be the viscosity of the solution.

- **Interionic attractions (solute-solute interaction)**

Electrolytic conductance decreases with increase in interionic attractions. This is because extent of dissociation will decrease with increase in solute-solute interaction. Hence, the number of ions in the solution for conduction will be less. Strong electrolytes dissociate completely due to low interionic attraction while weak electrolytes dissociate partially due to strong interionic attraction.

- **Solvation of Ions (solute-solvent interaction)**

Electrolytic conductance decreases with increase in solvation of ions. This is because solvation leads to an effective increase in the size of the ions as a result ion migrates at a slower rate. The smaller the size of the ion, the greater its solvation. This is the fact that Li^+ ion migrates at a slower rate than Na^+ ion because Li^+ ion is solvated more and hence, its effective size is greater than Na^+ .

- **Temperature**

Electrolytic conductance increases with increase in temperature. As the temperature increases, all the above three factors (i.e., viscosity, interionic attractions, and solvation) decrease in magnitude. As a result, dissociation, and average kinetic energy of ions of the electrolyte increases with increase in temperature. Consequently, electrolytic conduction increases with rise in temp.

- **Concentration of electrolyte**

Higher concentration of solute in a solution lead to decrease in electrolytic conduction. This is due to strong interionic interaction. Hence, electrolytic conductance increases on dilution.



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2.4.3 Conductance of Electrolytic Solutions

Before we study about the conductance of electrolytic solutions, a brief description of Ohm's law, resistance, resistivity, and conductance is desirable.

- **Ohm's Law**

According to this law, the potential difference '**V**' applied across a conductor is directly proportional to the strength of current '**I**' that flows through conductor, provided all physical conditions constant.

$$\mathbf{V} \propto \mathbf{I} \quad \text{OR} \quad \mathbf{V} = \mathbf{I} \times \mathbf{R}$$

Where, R is proportionality constant called resistance and has unit ohm (Ω).

- **Resistance (R) and Resistivity (ρ)**

The resistance (R) of a conductor is taken as 1 Ω when a potential difference of 1 V is applied across it and a current of 1 ampere flows through it.

$$\mathbf{R} = \frac{\mathbf{V}}{\mathbf{I}} \quad \text{OR} \quad \text{ohm} = \frac{\text{Volt}}{\text{ampere}}$$

Resistance of a conductor can be measured with the help of a **Wheatstone bridge**. The resistance of any conductor or electrolyte is directly proportional to the length (l) and inversely proportional to the area of cross-section (a).

$$\mathbf{R} \propto \mathbf{l} \text{-----(i)} \quad \text{and} \quad \mathbf{R} \propto \frac{1}{\mathbf{a}} \text{-----(ii)}$$

$$\mathbf{R} \propto \frac{\mathbf{l}}{\mathbf{a}}, \quad \mathbf{R} = \rho \frac{\mathbf{l}}{\mathbf{a}} = \rho \frac{1 \text{ cm}}{1 \text{ cm}^2}$$

Here, ρ is known as **specific resistance or resistivity**. It is defined as the resistance of that conductor having its length equal to 1 cm and area of cross-section equal to 1 cm^2 .

Units: $\rho = \mathbf{R} \frac{\mathbf{a}}{\mathbf{l}} = \Omega \frac{1 \text{ cm}^2}{1 \text{ cm}} = \Omega \text{ cm}$

- **Conductance (G)**

It is the ease with which the electric current flows through the conductor or electrolyte. It is denoted by 'G' and is reciprocal of the resistance.

$$\mathbf{G} = \frac{1}{\mathbf{R}} \quad \text{Units:} \quad \mathbf{G} = \frac{1}{\Omega} = \Omega^{-1} \text{ or } \mathbf{S}$$

Written as : **ohm⁻¹** or **mho** or **siemen (S)**

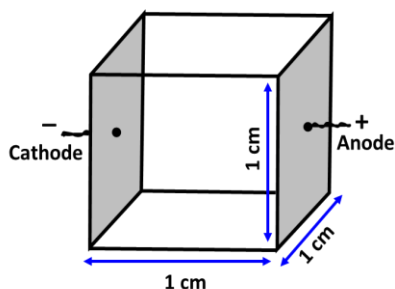
- **Conductivity (κ)**

Specific conductance or conductivity is reciprocal of the resistivity. It is denoted by the Greek symbol, kappa ' κ .'

$$\kappa = \frac{1}{\rho} \quad \text{Units:} \quad \kappa = \frac{1}{\Omega \text{ cm}} = \Omega^{-1} \text{ cm}^{-1} \text{ or } \mathbf{S} \text{ cm}^{-1}$$

Written as : **ohm⁻¹ cm⁻¹** or **mho cm⁻¹**

2.4.4 Conductivity or Specific conductance of electrolytic solutions



$$\kappa = \frac{1}{\rho} \text{ ----- (i)} \quad \rho = R \frac{a}{l} \text{ ----- (ii)}$$

Put value of eq (ii) in eq (i), we get, $\kappa = \frac{1}{R} \frac{l}{a}$

As we know : $\frac{1}{R} = G$ and $\frac{l}{a} = \text{cell constant } (G^*)$

So that, $\kappa = G \times G^* = \text{Conductance} \times \text{Cell constant}$

$$\therefore \kappa = G \frac{l}{a} \quad \text{or} \quad \kappa = G \frac{1 \text{ cm}}{1 \text{ cm}^2}$$

In case of electrolytic solution, the conductivity (κ) is the conductance (G) of the electrolyte when the solution is placed between two such electrodes which are 1 cm apart and each has an area of cross-section equal to 1 cm².

OR

Conductivity (κ) is the conductance (G) of 1 cm³ of the electrolytic solution.

The specific conductivity (κ) of solutions of different electrolytes in the same solvent and at a given temperature differs due to:

- size and charge of the ions in which they dissociate,
- ease with which the ions move under a potential gradient
- the concentration of ions.

Therefore, it becomes necessary to define a physically more meaningful quantity such as concentration conductivity i.e., **molar conductivity and equivalent conductivity**.

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2.4.5 Molar Conductivity and Equivalent Conductivity

- **Molar conductivity (λ_m)**

It can be defined as the conductance of all the ions present in electrolytic solution containing 1 mole of the electrolyte. It is denoted by Greek symbol, lambda (λ_m).

$$\lambda_m = \frac{\kappa \times 1000}{C_m} \text{ S cm}^2 \text{ mol}^{-1} \quad \text{OR} \quad \lambda_m = \frac{\kappa}{C_m \times 1000} \text{ S m}^2 \text{ mol}^{-1}$$

Here, C_m is Molar concentration or Molarity.

- **Equivalent conductivity (λ_{eq})**

It can be defined as the conductance of all the ions present in electrolytic solution containing 1 gram equivalent of the electrolyte. It is denoted by lambda (λ_{eq}).

$$\lambda_{eq} = \frac{\kappa \times 1000}{C_{eq}} \text{ S cm}^2 \text{ (gm.eq.)}^{-1} \quad \text{OR} \quad \lambda_{eq} = \frac{\kappa}{C_{eq} \times 1000} \text{ S m}^2 \text{ (gm.eq.)}^{-1}$$

Here, C_{eq} is Normality.

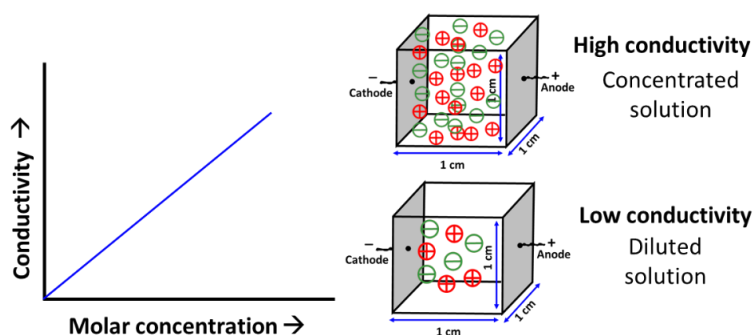
- **Relationship between λ_m and λ_{eq}**

$$\frac{\lambda_m}{\lambda_{eq}} = \frac{\frac{\kappa \times 1000}{C_m}}{\frac{\kappa \times 1000}{C_{eq}}} = \frac{C_{eq}}{C_m} = \frac{N}{M} = \frac{M \times n_{\text{factor}}}{M} = n_{\text{factor}}$$

$$\lambda_m = \lambda_{eq} \times n_{\text{factor}}$$

2.5 Variation of Conductivity (κ) and Molar conductivity (λ_m) with concentration of the electrolytic solution

2.5.1 Variation of Conductivity (κ) with concentration



The conductivity (κ) or specific conductance always decreases with a decrease in the concentration of both weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decrease on dilution.

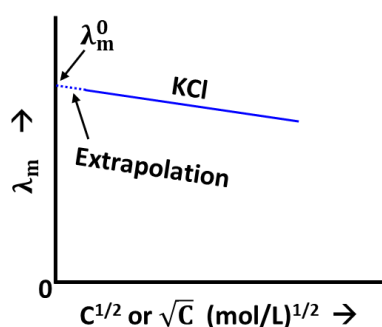
The conductivity of the strong electrolyte is expected to be more because it is almost completely ionized in solution. Conversely, the weak electrolyte is expected to have a lower conductivity due to less ionization.

2.5.2 Variation of Molar conductivity (λ_m) with concentration

Strong electrolyte shows small increase in molar conductivity whereas weak electrolyte shows sharp increase in molar conductivity with the decrease in concentration.

• In Strong Electrolyte

Strong electrolytes (ie, NaCl, KCl, NaOH etc.) ionise almost completely in aqueous solution. Upon dilution, their molar conductivity shows very small increase. This slight increase is due to a decrease in the inter-ionic attraction and, therefore, an increase in the molar conductivity resulting from an increase in ionic mobility.



This increase in molar conductivity will continue until inter-ionic attractions become negligible and a further increase in dilution is not likely to change the molar conductivity of the electrolyte. This is known as **limiting molar conductivity**. It is denoted as λ_m^∞ or λ_m^0 (molar conductance at infinite dilution or at nearly zero concentration of solution). The value of λ_m^0 can be obtained by extrapolation.

Mathematical relationship between the molar conductivity at any concentration and the molar conductivity at infinite dilution is known as **Debye Huckel-Onsagar equation**.

$$\lambda_m = \lambda_m^0 - A\sqrt{C}$$

Here, λ_m = Molar conductivity at any concentration

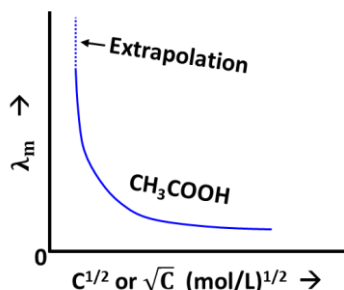
λ_m^0 = Molar conductivity at infinite dilution or at nearly zero concentration

A = Constant depending upon the nature of solvent and temperature

C = Molar concentration of the electrolyte

• In Weak Electrolyte

Weak electrolytes (ie, CH_3COOH , NH_4OH etc.) do not ionise completely in aqueous solution. Upon dilution, there is a sharp increase in molar conductivity due to an increase in the ionization of the weak electrolyte. Thus, the increase in ionisation results in the increase in number of ions in solution.



Since the curve for a weak electrolyte does not become linear at any stage, it is not possible to obtain the limiting molar conductivity (λ_m^0) by extrapolating the curve to zero concentration. The problem was solved with the help of **Kohlrausch's law**.

2.5.3 Kohlrausch's Law

According to this law, at infinite dilution (when the dissociation is complete) each ion of an electrolyte makes a definite contribution to the total molar conductivity, irrespective to the nature of the other ion with which it is associated. The individual contribution of an ion towards the total molar conductivity of the electrolyte is called **ionic conductivity**.

Thus, Molar conductivity of the electrolyte at infinite dilution is the sum of cationic conductivity and anionic conductivity.

$$\lambda_m^0 = \lambda_{\text{cation}}^0 + \lambda_{\text{anion}}^0$$

For example, consider an electrolyte (A_xB_y), it will ionise as ;



The molar conductivity at infinite dilution (λ_m^0) is expressed as :

$$\lambda_m^0 = \lambda_{\text{A}_x\text{B}_y}^0 = x\lambda_{\text{A}^{+y}}^0 + y\lambda_{\text{B}^{-x}}^0$$

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Applications of Kohlrausch's Law

- Calculation of λ_m at infinite dilution for weak electrolytes**

The molar conductivity of Acetic acid (CH_3COOH) can be found if the molar conductivities at infinite dilution of strong electrolytes (HCl , CH_3COONa and NaCl) are known.

$$\lambda_{\text{CH}_3\text{COOH}}^0 = \lambda_{\text{HCl}}^0 + \lambda_{\text{CH}_3\text{COONa}}^0 - \lambda_{\text{NaCl}}^0$$

OR

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

- Calculation of degree of dissociation of weak electrolytes**

Molar conductivity of a weak electrolyte depends upon its degree of dissociation. Higher the degree of dissociation, greater the number of ions in the solution, hence the higher the molar conductivity. When the dissociation of the electrolyte on dilution is almost complete, the degree of dissociation reaches unity (1).

Thus,

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Molar conductivity at given concentration } (\lambda_m^c)}{\text{Molar conductivity at infinite dilution } (\lambda_m^0 \text{ or } \lambda_m^\infty)}$$

Further, dissociation constant ' K_d ' at given concentration ' C ,' for weak electrolyte ' AB ' can be calculated from the degree of dissociation, as follow:

	AB	\rightleftharpoons	A⁺	+	B⁻
Initial Conc. (mol/L)	C		0		0
Final Conc. (mol/L)	C-C α		C α		C α

$$K_d = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = \frac{C\alpha \cdot C\alpha}{C-C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If an electrolyte dissociates into 'n' number of ions, then ;

$$K_d = \frac{C^n\alpha^n}{C(1-\alpha)} = \frac{C^{n-1}\alpha^n}{1-\alpha}$$

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Exercises

1. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100Ω . If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520Ω . Calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S/m .
2. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity, and molar conductivity.
3. The conductivity of $0.001028 \text{ mol L}^{-1}$ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.
4. The molar conductivity of 0.025 mol L^{-1} methanoic acid is $46.1 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda_{(\text{H}^+)}^\circ = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda_{(\text{HCOO}^-)}^\circ = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$.
5. A solution of CuSO_4 is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?
6. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?
7. A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?
8. Three electrolytic cells A, B, and C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are 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?

The logo for Dev Academy features the word "Dev" in a white serif font inside a white circle, followed by the word "Academy" in a white cursive script font, all set against a black background.

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Part – 3

3.1 Some Commercial Batteries or Cells

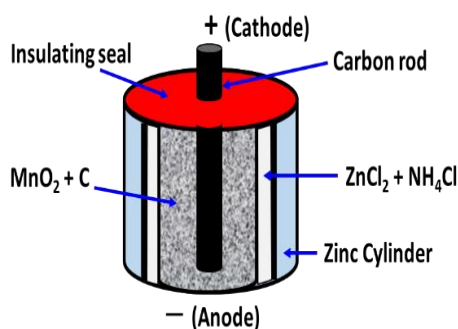
Any battery (may have one or more than one cell connected in series) or cell that can be used as a source of electrical energy is basically an electrochemical cell. There are mainly three types of cells **(a)** Primary cells **(b)** Secondary cells **(c)** Fuel cells

3.1.1 Primary Batteries

Primary batteries are **non-rechargeable**. Therefore, the reaction occurs only once and cannot be reversed by passing an electric current through the cell.

a) Dry cell (or Leclanche cell)

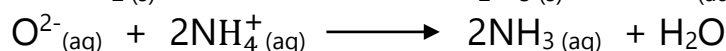
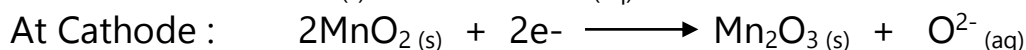
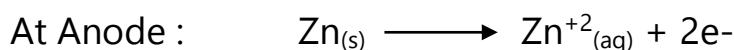
It is most familiar commercial cell, generally used in torches, toys, transistors and many other devices.



Construction :

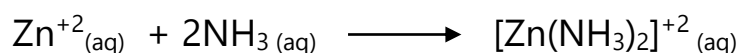
It consists of a zinc cylinder filled with a paste of NH_4Cl and little of ZnCl_2 . The zinc cylinder acts as **anode**. A carbon or graphite rod placed in the centre of the cylinder but not touching the base and surrounded by a black paste of MnO_2 . The carbon rod act as **cathode**. The opening of the cylinder is covered with a rubber seal.

Chemical Reactions :



A dry cell generates voltage between **1.25 to 1.5 volt**.

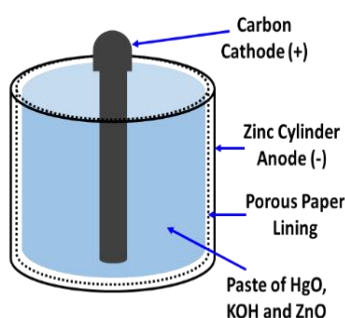
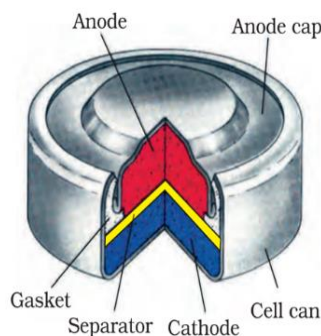
In MnO_2 the Mn^{+4} ions get reduced to Mn^{+3} ions and form Mn_2O_3 . Ammonia so liberated combines with Zn^{+2} ions to form complex ions, diamminezinc(II) cation $[\text{Zn}(\text{NH}_3)_2]^{+2}$.



b) Mercury Cell

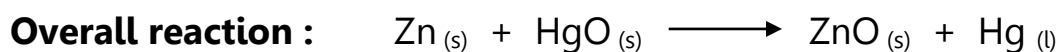
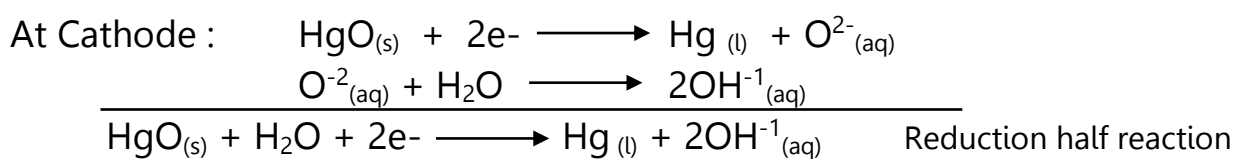
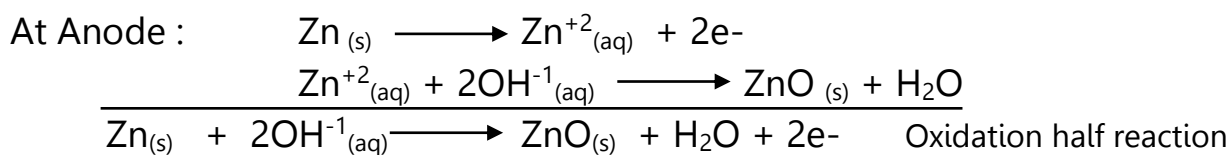
This is another type of dry cell which is suitable for low current devices such as hearing aids, watches, cameras etc.

Construction:



Amalgamated Zinc (Zn/Hg) container acts the anode (-), and a paste of HgO and carbon acts as the cathode (+). The electrolyte is a paste of KOH and ZnO filled between the two electrodes. A lining of porous paper keeps electrolyte separated from the Zinc anode.

Chemical Reactions



The overall reaction does not involve any ion whose concentration can change; therefore, the cell gives a constant potential of **1.35 volt** throughout its life.

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3.1.2 Secondary Batteries

Secondary batteries are **rechargeable**. Therefore, the reaction can be reversed by passing an electric current through the cell.

Two well-known examples of secondary cells are:

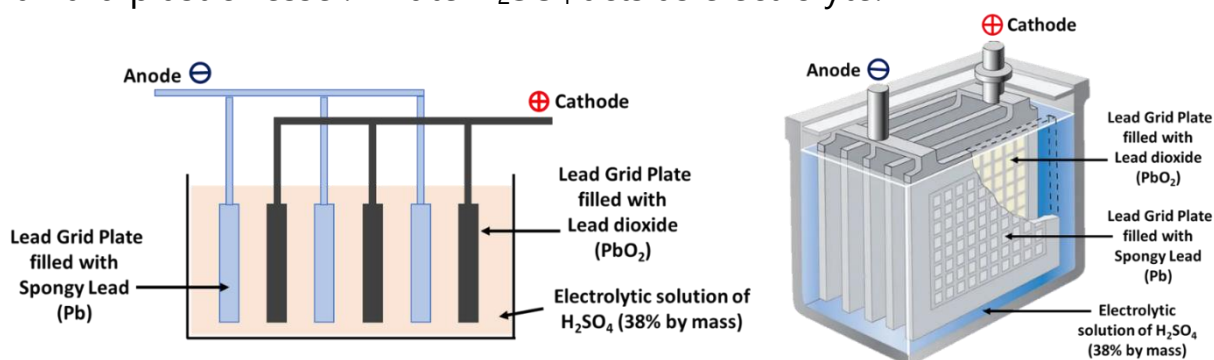
- (i) Lead storage battery (ii) Nickel-cadmium storage battery

a) Lead Storage Battery

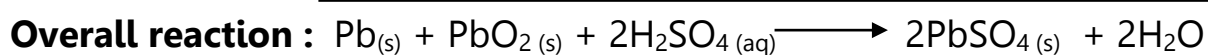
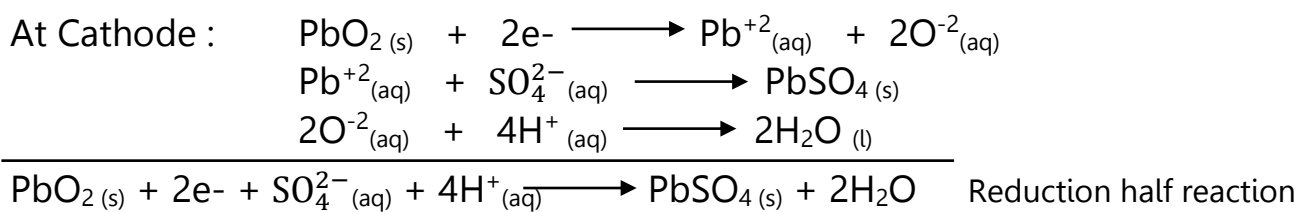
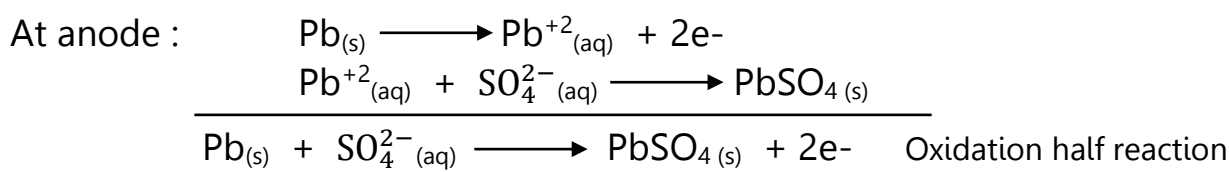
It is most frequently used battery in automobiles and inverters. As the voltage of individual cell is only **2 volts**, therefore, 3 or 6 such cells are joined in series to get a **6-volt or 12-volt battery**.

Construction:

The anode is made up of **lead**. The cathode is made up of **lead dioxide (PbO₂)**. Cathode plates and anode plates are separated by thin perforated plastic or fibre glass sheets. The whole arrangement is dipped in electrolytic solution of dilute H₂SO₄ (38% by mass and having density 1.31 gm/ml) taken in a hard plastic vessel. Dilute H₂SO₄ acts as electrolyte.



Chemical Reactions : (During Discharging or working)

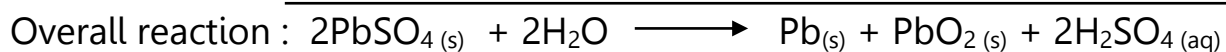
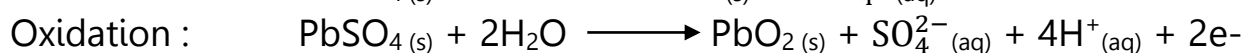
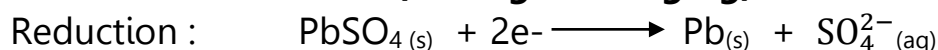


From the above reaction during working of the cell, PbSO_4 is formed and H_2SO_4 is used up. Therefore, the density of H_2SO_4 falls. The battery needs to be charged when the density of H_2SO_4 falls below 1.2 gm/mL.

Recharging the Battery:

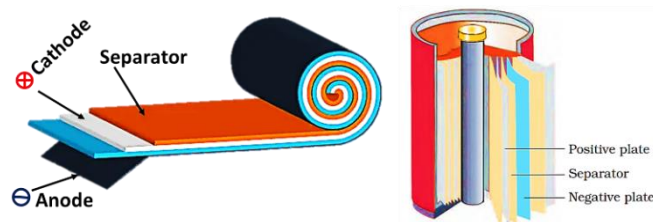
It can be charged by connecting it to an external source of direct current. Recharging is possible in this case because the PbSO_4 formed during the working of cell is a solid and sticks to the electrodes. Therefore, it can lose or gain electrons during electrolysis.

Chemical Reactions : (During Recharging)



b) Nickel-Cadmium Storage Battery

It has a larger life than the lead storage battery but it is more expensive to manufacture. The maximum voltage of this cell is 1.4 volt and is used in calculators, cameras, and electric shavers etc.

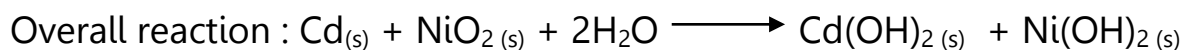
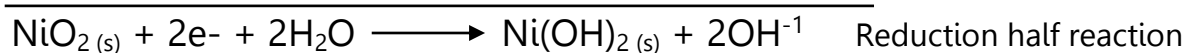
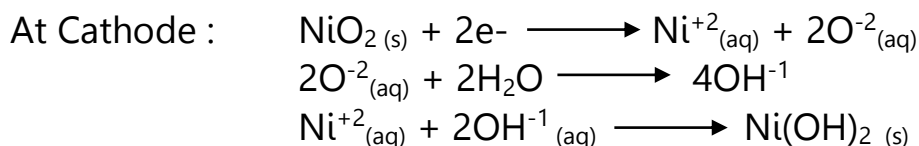
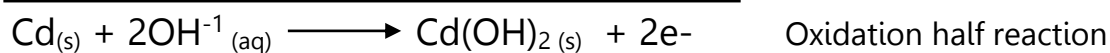
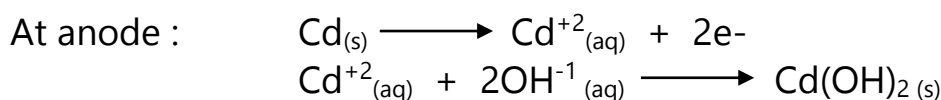


Construction

The anode consists of several Cadmium metal. The cathode consists of a metal grid packed with **Nickel dioxide (NiO_2)**.

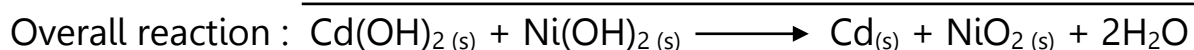
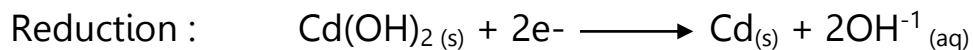
The electrolyte in this cell is KOH.

Chemical Reactions : (During Discharging or working)



As after discharging products formed are solid, they adhere to the electrodes. Hence, the reaction can be reversed during charging. Further, as no gases are produced during charging or discharging, the cell can be sealed.

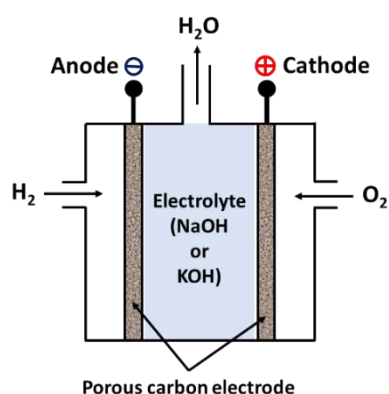
Chemical Reactions : (During Recharging)



3.1.3 Fuel Cells

Fuel cells are devices designed to directly convert energy from the combustion of fuels (such as hydrogen or hydrocarbons) into electrical energy.

Hydrogen-Oxygen (H₂-O₂) Fuel Cell :



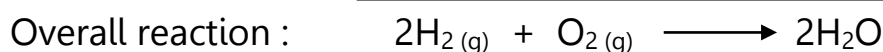
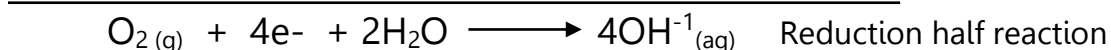
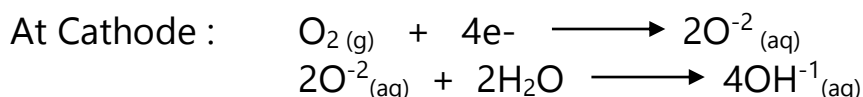
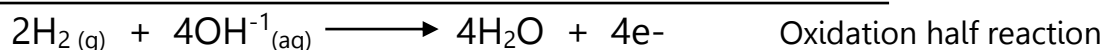
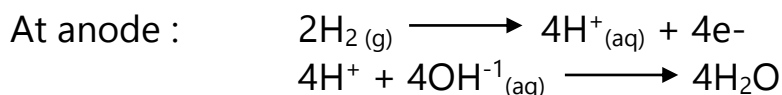
Construction :

In the cell, hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated KOH or NaOH solution. Catalysts (such as Pt, CoO, Ag, Pd etc.) are incorporated in the electrodes to accelerate the electrode reaction.

The H₂-O₂ fuel cell is also known as **Bacon cell**.

The cell works continuously if the gases H₂ and O₂ are supplied continuously at 50 atm and at a temperature of 525 K.

Chemical Reactions :



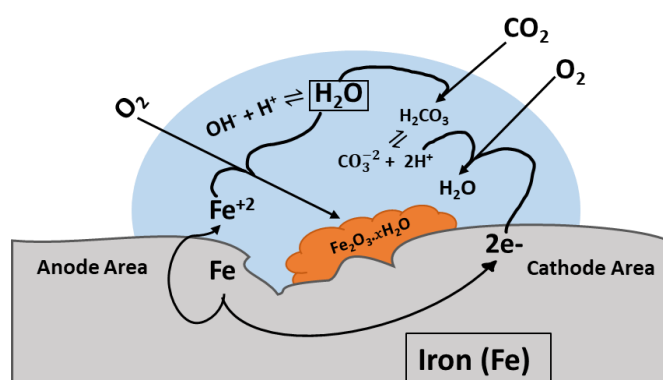
3.2 Corrosion

Corrosion is the phenomenon when metals are exposed to air and water vapour, their surfaces are slowly eaten up due to the formation of certain **ore-like compounds** (i.e., metal oxide, metal carbonates, metal sulphides etc.). In case of Iron, corrosion is called **rusting**. Iron rust is hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) and brown in colour.

Tarnishing of silver, development of green coating on copper and bronze are some other examples of corrosion.

3.2.1 Mechanism of Corrosion (Rusting of Iron) :

The actual mechanism of rusting is in fact a complicated process which is not fully understood. Several theories have been proposed, one of these is the **electrochemical theory**.

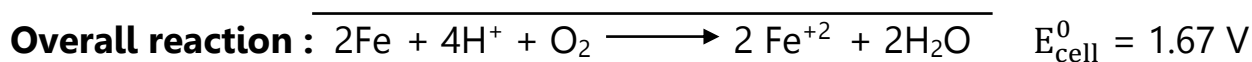
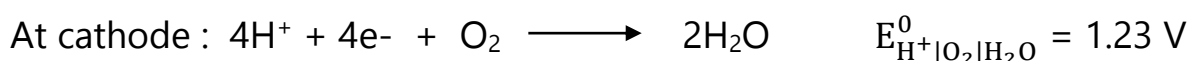
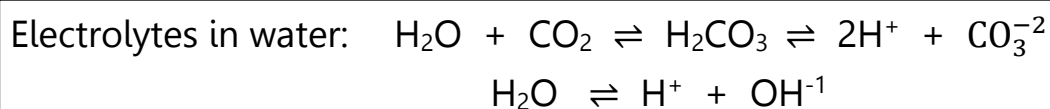


It suggests that the uneven surface of iron behaves like small electrochemical cell in the presence of water. Gases like CO_2 and O_2 dissolved in water and this water serves as the electrolytic solution.

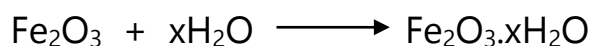
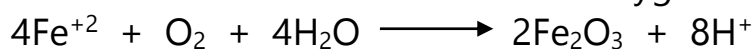
Chemical Reactions :



Due to the accumulation of these electrons, the rest of the metal behave as cathode.



The Fe^{2+} ions formed in reaction is further react with oxygen to form rust and H^+ ion.



The hydrated ferric oxide once formed acts as a catalyst for further oxidation of the fresh metal.



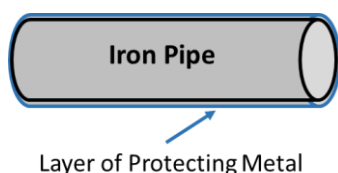
3.2.2 How to Prevent Corrosion ?

- **Barrier Protection**

It is the simplest method in which metal surface is not allowed to come in contact with O_2 , CO_2 or Water. This can be achieved;

- ✓ by painting the surface of metal
- ✓ by coating the metal surface with a thin film of oil or grease or bisphenol.
- ✓ by electroplating the metal with non-corrosive metals like Ni, Cr or Sn.

- **Sacrificial Protection**

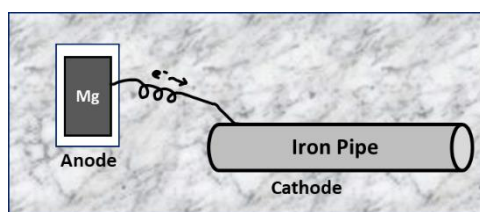


In this method, Iron objects (or metal which is to be protected) are covered with a protective film of more electropositive metals like Zn, Mg, etc. Therefore, more electropositive metal sacrifice itself to protect the iron.

The best example of this type is **Galvanization**:

In the case of galvanized articles, zinc layer deposited on Iron, react with O_2 and CO_2 forms an invisible protective layer of basic zinc carbonate $\text{ZnCO}_3 \cdot \text{Zn}(\text{OH})_2$, which protects the metal from corrosion.

- **Electrical Protection (Cathodic protection)**



This method is used for the protection of submerged iron objects like sewer pipes, storage tanks, ships, etc. The exposed metal surface of Iron is protected by connecting it to a block of more electropositive metal (i.e., Mg, Al, Zn etc.) by a piece of wire.

In this system, Iron acts as cathode while the protecting metal acts as anode.



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