Chapter-12

ELECTROCHEMISTRY

"The branch of chemistry, which deals with the <u>study of</u> <u>inter-conversion of chemical and electrical energies</u> is called electro chemistry".

Conductors:

The substances which conduct current due to the movement of free electrons with no chemical change in them, are called conductors.

All metals e.g. Cu, Ni, Fe etc and one of non-metals like $C_{(graphite)}$ are conductors.

Electrolytes:

The substances whose aqueous solutions or molten states conduct electricity due to movements of ions with chemical change in them, are called electrolytes. They conduct electricity due to movement of their free ions.

Strong electrolyte:

A substance which completely dissociates into ions and conducts more current is called strong electrolyte. A strong electrolyte could be a strong acid or strong base or highly ionizable salt.

e.g. HCl, NaOH, NaCl respectively.

Weak electrolyte:

A substance which only partially dissociates into ions and conducts less current is called weak electrolyte. A weak electrolyte could be a weak acid or weak base or less ionizable salt. e.g. CH₃COOH, NH₄OH, Na₂CO₃ respectively.

Non-electrolyte:

A substance which do not dissociates into ions in aqueous solutions and does not conduct current is called non-electrolyte e.g. sucrose, glucose, fructose, urea etc.

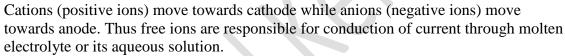
Electrolysis:

The process of decomposition of an electrolyte by passage of electricity through molten or aqueous solution of the electrolyte is called electrolysis.

Electrolytic Conduction:

When an electrolyte is dissolved in water or is melted it dissociates into ions which become free to move.

When electricity passes, ions move towards their respective electrodes.





Oxidation:

"Addition of oxygen"

Or

"Removal of hydrogen"

Or

"Loss of electrons"

Or

"Increase in oxidation number" is called oxidation

Reduction:

"Removal of oxygen"

Or

"Addition of hydrogen"

Or

"Gain of electrons"

Or

"Decrease in oxidation number" is called reduction

Oxidizing Agent:

The substance which oxidizes other substances and itself gets reduced in the reaction is called oxidizing agent e.g. KMnO₄ and K₂Cr₂O₇ are strong oxidizing agents.

Reducing Agent:

The substance which reduces other substances and itself gets oxidized in the reaction is called reducing agent e.g. H₂S and SO₂ are reducing agents.

Oxidation Number or Oxidation State:

Apparent charge +ve or –ve which appears on an atom of a molecule due to difference of electronegativity is called oxidation number.

Rules for assigning the Oxidation Numbers:

- (i) Oxidation number of an atom in elemental state is zero. e.g H₂, O₂, O₃, P₄, S₈, N₂, C, Na, He etc, they all have zero oxidation number.
- (ii) Oxidation number of Group-I metals (Li, Na, K, Rb, Cs) in their compounds is +1.
- (iii) Oxidation number of Group-II metals (Be, Mg, Ca, Sr, Ba) in their compounds is +2.
- (iv) Oxidation number of Hydrogen in its compounds is +1 except metal hydrides (NaH, CaH₂ etc). In these metal hydrides the oxidation number of hydrogen is -1 due to greater electronegativity of hydrogen as compared to metals.
- (v) Oxidation number of Oxygen in its compounds is -2 except:
 - (a) peroxides (H₂O₂, Na₂O₂, BaO₂), in peroxides oxygen has oxidation number -1 $H^{\delta +} O^{\delta -} O^{\delta -} H^{\delta +}$
 - (b) superoxides (KO₂, RbO₂, CsO₂), in superoxides oxygen has oxidation number ½
 - (c) Oxiflurides. In OF_2 oxidation number of oxygen is +2, in O_2F_2 oxidation number of oxygen is +1 in O_2F_2 .
- (vi) Oxidation number of halogens in their binary compounds (NaCl, CaCl₂, AlCl₃, KBr, BaI₂ etc) is -1. except interhalogens.

Inter halogens FCl, in it F has oxidation number -1 while Cl has +1.

 ClF_3 , in it F has oxidation number -1 while Cl has +3.

 BrF_5 , in it F has oxidation number -1 while Br has +5.

IF₇, in it F has oxidation number -1 while I has +7.

- (vii) Oxidation number of ion as a whole (i.e. sum of oxidation numbers of all atoms in the ion) is same as is charge on the ion e.g. as a whole oxidation number of OH ion is -1.
- (viii) Oxidation number of a molecule as a whole (i.e. sum of oxidation numbers of all atoms in the molecule) is zero. e.g. as a whole oxidation number of H₂O molecule is zero.

Balancing of Chemical Equations:

A complete balance equation is the one in which all atoms, charges as well as gain and loss of electrons are balanced.

There are three methods of balancing chemical equations.

- (i) Inspection method
- (ii) Redox method
- (iii) Ion and electron method

Redox Method or Oxidation Number Method:

This method involves following steps.

- (i) Write down oxidation numbers of all atoms of all molecules.
- (ii) Point out the atoms whose oxidation numbers are changed by finding their oxidation numbers per their atoms. Such atoms whose oxidation numbers are changed are called significant atoms.
- (iii) Find the gain and loss of electrons first per atom then per molecule or per ion.
- (iv) Balance the gain and loss of electrons by multiplying the oxidizing agent and/or reducing agent by some suitable number(s).
- (v) Now balance the significant atoms.
- (vi) Balance the charge if any by adding H⁺ ions in case of acid medium and OH⁻ ions in case of basic medium.
- (vii) Now balance the remaining atoms and add water if needed.

Ion and Electron Method or Half Reaction Method:

It involves following steps.

- (i) Divide the equation into two half reactions i.e. oxidation half and reduction half.
- (ii) Balance each half reaction separately as follows:
 - (a) Balance atoms other than hydrogen and oxygen.
 - (b) Now balance hydrogen and oxygen:

<u>In acid medium</u>: First balance oxygen by adding H₂O and then balance hydrogen by adding H⁺ ions.

<u>In basic medium</u>: Balance oxygen and hydrogen simultaneously by adding

H₂O and OH ions. Add one water for each excess oxygen on same side and double hydroxyl on other side both oxygen and hydrogen will be balanced. If hydrogen is still not balanced then to adjust hydrogen, add one hydroxyl ion for each excess hydrogen on same side and same number of water on other side.

- (c) Find net charge on both sides of the equation and balance it by adding electrons.
- (iii) After balancing both half reactions separately then balance the gain and loss of electrons by multiplying one half or both half reactions by some suitable number(s).
- (iv) Add the two half reactions and cancel the species appearing on both sides.

Electrodes:

The plates, wires or rods through which the current enters or leave the electrolyte in a cell, are called electrodes. Electrodes are usually metals but graphite (a non-metal) is also electrode.

Electrodes are of two types.

(i) **Anode:**

The electrode through which electrons leave the cell is called anode.

(ii) **Cathode:**

The electrode through which electrons enter the cell is called cathode.

Faraday's Laws of Electrolysis:

Michael Faraday in 1813 gave two laws.

First Law of Electrolysis:

This law states, "The quantity of substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed."

W	∞	Q
---	----------	---

But
$$Q = I t$$

Or
$$W = Z I t$$

Whereas

W = mass of substance liberated

Q = quantity of electricity in coulombs

I = strength of current in amperes

t = time in seconds

Z = proportionality constant known as electrochemical equivalent

Explanation:

The quantity of electricity is measured in coulombs. One coulomb charge passes through every point in a circuit in which a current of one ampere flows for one second.

 $Coulombs = Amperes \ x \ Seconds$

$$Q = I x t$$

Hence quantity of electricity (Q in coulombs) is a product of current (I in amperes) and time (t in seconds).

An ampere is defined as "the current which liberates 0.001118 g of silver (electrochemical equivalent of silver) or 0.0003295 g of copper (electrochemical equivalent of copper) from the solution of these ions as a result of electrolysis."

Electrochemical equivalent of a substance is defined as "the mass of a substance produced when one ampere current is passed through the solution of ions of the substance in one second."

Or

"the mass of a substance produced when one coulomb charge is passed through the solution of ions of the substance."

Mass of silver produced when <u>one coulomb</u> charge is passed through solution of Ag^+ ions = 0.001118 g = (Z) Mass of silver produced when <u>two coulomb</u> charge is passed through solution of Ag^+ ions = 0.001118 g x 2 coulomb

It means that the mass of substance produced = electrochemical equivalent of substance x charge in coulomb

That is $W = Z \times Q$

But Q = I x t

Therefore $W = Z \times I \times t$

Second Law of Electrolysis:

This law states, "When same quantity of electricity passes through different electrolytes, the masses of different substances produced at the electrode are in the ratio of their chemical equivalents."

Or

"When same quantity of electricity passes through different electrolytes, the masses of different substances produced at the electrode are directly proportional to their equivalent masses."

Relative atomic mass (Ar) of the element (in a.m.u)

Equivalent mass of an element =

Electrovalency of the element

- e.g. (i) Equivalent mass of $Na^+ = 22.989 / 1 = 22.989$ a.m.u.
- e.g. (ii) Equivalent mass of $Ag^+ = 107.868 / 1 = 107.868$ a.m.u.
- e.g. (iii) Equivalent mass of $Cu^{+2} = 63.546 / 2 = 31.773$ a.m.u.

"Equivalent mass expressed in grams is called gram-equivalent."

- e.g. (i) 22.989 g of sodium is 1 gram-equivalent of sodium.
- e.g. (ii) 107.868 g of silver is 1 gram-equivalent of silver.
- e.g. (iii) 31.773 g of copper is 1 gram-equivalent of copper.

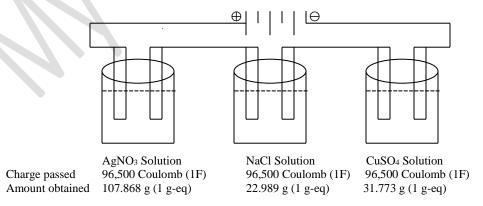
Consider reaction Na⁺+ e⁻ \rightarrow Na

This shows the charge required to discharge one sodium ion is 1.6 x 10⁻¹⁹ coulomb while the charge required to discharge one mole sodium ion will be 1.602 x 10⁻¹⁹ X 6.023 x 10²³ coulomb.

It means charge required to liberate 22.989 a.m.u. of sodium = 1.6×10^{-19} coulomb Then, charge required to liberate 22.989 g of sodium = $1.6 \times 10^{-19} \times 6.023 \times 10^{23} = 96488$ coulombs

Thus the charge required to liberate 1 gram-equivalent of a substance is 96,488 coulombs and it is roughly taken as 96,500 coulombs or 1 Faraday.

So 1 Faraday (F) liberates 1 gram-equivalent of the substance. Thus on passing same quantity of electricity through different electrolytes, same number of gram-equivalents will be produced.



According to Faraday's First Law W ∝ I t

According to Faraday's Second Law W ∝ chemical equivalent (e)

On combining $W \propto I t x e$

Or W = constant x I t e

Constant of this proportionality is 1 / F

Therefore $W = \frac{I t e}{-}$

Where as F = Faraday constant = 96,500 coulombs

I = current in amperes

t = time in seconds

e = equivalent mass in grams

One Faraday is defined as "the quantity of electricity required to liberate 1 gram-equivalent of any element."

Electrode Potential:

In 1791, an Italian Professor of anatomy named Luigi Galvani noticed that the leg muscles of freshly dissected frog contracted when he touched the knife dipped in CuSO₄ solution. He shared his observation with another Italian professor of physics, Alessandro Volta. From this, Alessandro Volta, gave the idea that knife was charged when was placed in electrolytic solution (CuSO₄ solution). The charged knife gave electric shock to frog.

Alessandro Volta showed that when a metal rod is dipped in solution of its ions, it oxidizes to its ions and electrons are gathered on rod, due to which an electric potential develops on metal rod.

$$Zn = Zn^{2+} + 2e^{-}$$

 $Cu = Cu^{2+} + 2e^{-}$

The tendency to be oxidized is different for different metals and hence different potentials develop on different metals.

"The electric potential developed on an electrode when it is in equilibrium with its ions" is called electrode potential."

It is represented by letter 'E'.

Where as

"The electric potential developed on an electrode when it is in equilibrium with 1M solution of its ions at 298K is called standard electrode potential."

It is represented by letter 'E°'.

Types of Electrode potential:

Electrode potential is of two types i.e.

- > oxidation potential
- > reduction potential

oxidation potential

Oxidation potential:

"The tendency of a substance to be oxidized is called its oxidation potential."

Reduction potential:

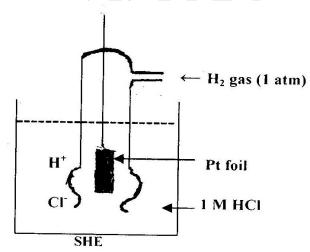
"The tendency of a substance to be reduced is its called reduction potential."

It is impossible to determine absolute electrode potential so we measure relative electrode potentials.

For this purpose various reference electrodes are used few reference electrodes are following. **Standard Hydrogen Electrode** is primary reference electrode while other are secondary reference electrodes.

(i) Standard Hydrogen Electrode (SHE):

Standard Hydrogen Electrode 'SHE' is a primary reference electrode.



Standard Hydrogen Electrode i.e. SHE consists of a platinum foil, which is coated electrolytically with finely divided platinum black and suspended in 1M HCl soln. It is enclosed in a glass tube as shown in figure. Pure hydrogen gas at 1atm is continually supplied to it. Electrode potential of hydrogen electrode is arbitrarily chosen as zero.

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^{o}_{Red} = 0.000 \text{ V}$$

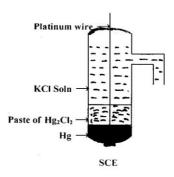
$$H_2 \rightarrow 2H^+ + 2e^- \qquad E^{o}_{Ox} = 0.000 \text{ V}$$

- ★ Although SHE is primary reference electrode but it is inconvenient to use because
 - (i) It is difficult to maintain the conc of HCl soln at 1M during use.
 - (ii) It is difficult to maintain the pressure of H₂ gas at 1atm during use.
 - (iii) Platinum get contaminated during use.

Hence secondary reference electrodes are used for determination of electrode potentials instead of SHE. However the electrode potentials of secondary reference electrodes are measured by SHE.

(ii) Standard Calomel Electrode 'SCE':

Standard Calomel Electrode 'SCE' is a secondary reference electrode.



It consists of a glass vessel with small quantity of pure mercury at the bottom. Above mercury, paste of mercurous chloride is placed and above the paste is saturated solution of KCl. A platinum wire is fused with mercury in glass vessel for making electrical contact. If saturated KCl solution is used then electrode is called Saturated Calomel Electrode (SCE) and if 1N KCl solution is used then electrode is called Normal Calomel Electrode (NCE) and if 0.1N KCl soln is used then electrode is called Decinormal Calomel Electrode (DNCE). The electrode potential changes with concentration of KCl. When KCl is saturated then electrode potential is 0.2415 V with reference to SHE.

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^ E^{\circ}_{Red} = +0.2415 \text{ V}$$

$$2Hg + 2Cl^{-} \rightarrow Hg_{2}Cl_{2} + 2e^{-}$$
 $E^{o}_{Ox} = -0.2415 \text{ V}$

Importance of Calomel Electrode:

- It is less prone to contamination.
- Its reproducibility is better than silver/silver chloride electrode.
- It is not toxic unless the glass vessel is broken.
- Below 50°C it gives good results however above this temperature it is not recommended to use as mercurous chloride breaks down and reading will not be stable.

(iii) Silver electrode:

Silver electrode is a secondary reference electrode.

AgCl is deposited electrolytically on silver wire and is immersed in silver chloride solution. its electrode potential is 0.2224 V with reference to SHE.

$$AgCl + e^- \rightarrow Ag + Cl^ E^{\circ}_{Red} = +0.2224 \text{ V}$$

$$Ag + Cl^- \rightarrow AgCl + e^- \qquad E^{\circ}_{Ox} = -0.2224 \text{ V}$$

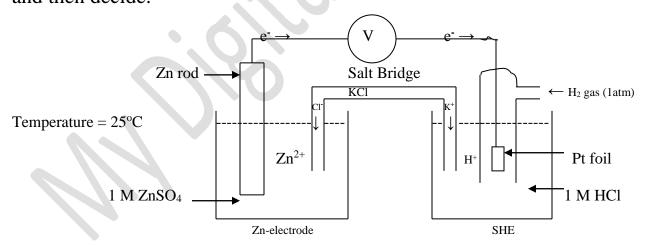
Measurements of Electrode Potential:

It is impossible to determine absolute electrode potential, so we measure relative electrode potential. For this purpose some reference electrode is used. Usually the reference electrodes are often used are SHE, SCE and Silver electrode. Out of which SHE is primary reference electrode while other are secondary reference electrodes.

Electrode potential of SHE is arbitrarily chosen as 0.000 V.

The electrode whose electrode potential is to be measured is connected with standard hydrogen electrode. A salt bridge is used between the two electrodes. Thus a galvanic or voltaic cell is established.

Potential difference is measured by voltmeter under standard conditions. It gives electrode potential of test electrode. If it is more than that of SHE then +ve sign will be given to it and if it is less than that of hydrogen then –ve sign will be given to it. To decide whether electrode potential of test electrode is more or less than that of hydrogen electrode, we note the direction of current that is the direction of flow of electrons and then decide.

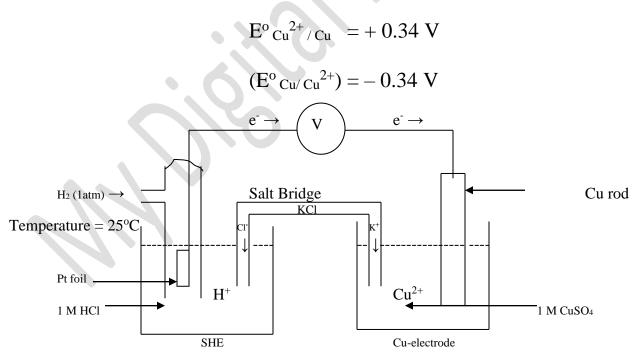


To measure the electrode potential of zinc electrode, a galvanic or voltaic cell is established between zinc electrode and standard hydrogen electrode. Reading on volt meter is taken under standard conditions. Volt meter reads 0.76V. Direction of current is from zinc electrode to hydrogen electrode, it means oxidation occurred at zinc electrode so its oxidation potential is higher than that of hydrogen electrode by 0.76 volt. Thus oxidation potential of zinc electrode is + 0.76 V while its reduction potential will be - 0.76 V.

$$E^{o}_{Zn/Zn}^{2+} = +0.76 V$$

$$(E^{o}_{Zn}^{2+}/_{Zn}) = -0.76 \text{ V}$$

Similarly to measure the electrode potential of copper electrode, a galvanic or voltaic cell is established between copper electrode and standard hydrogen electrode. Reading on volt meter is taken under standard conditions. Volt meter reads $0.34\,\mathrm{V}$. Direction of current is from hydrogen electrode to copper electrode, it means reduction occurred at copper electrode so its reduction potential is higher than that of hydrogen electrode by $0.34\,\mathrm{volt}$. Thus reduction potential of copper electrode is $+0.34\,\mathrm{V}$ while its oxidation potential will be $-0.34\,\mathrm{V}$.



The Electrochemical Series:

A list in which elements are arranged according to their standard electrode potentials is called electrochemical series.

Often elements are arranged in increasing order of standard reduction potentials.

Applications:

- (i) Calculation of voltage or e.m.f. of cell: Noting reduction or oxidation potentials from electrochemical series cell voltage or e.m.f. of the cell is calculated.
- (ii) Prediction of feasibility of a chemical reaction: It is used to predict whether a particular reaction will occur or not. If E°_{Cell} or e.m.f. of the reaction, calculated by summation of E° values of two half cell reactions is +ve then reaction is feasible but if it is –ve then reaction is not feasible.

Consider reaction $Cu + Zn^{+2} \rightarrow Cu^{+2} + Zn$

$$E^{o}{}_{zn^{+2}/\;zn} - E^{o}{}_{cu^{+2}/\;cu} = (-0.76) - \; (+0.34) \; = -1.10V$$

as E°cell of the reaction is –ve so reaction is not feasible.

Now consider reaction $Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$

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

as its e.m.f is +ve so this reaction is feasible.

- (iii) **Prediction of Cell:** If e.m.f the cell is +ve then it is spontaneous but if its e.m.f. is –ve then it is non-spontaneous. Voltaic cells are spontaneous while electrolytic cells are non-spontaneous.
- (iv) Prediction of an element to be oxidizing agent or reducing agent: An element having higher reduction potential or the one listed below hydrogen in the electrochemical series, will be reduced and will act as oxidizing agent and vice versa e.g. Cu⁺² having higher reduction potential (+0.34 V) so it will be reduced and acts as oxidizing agent while Zn⁺² has lower reduction potential (-0.76 V) so it will be oxidized and acts as reducing agent.
- (v) Prediction of reactivity of metals: Metal having higher reduction potential has low tendency to lose electrons so low will be its reactivity and vice versa. e.g $E^{o}_{Ag^{+1}/Ag} = +0.7994$ V while $E^{o}_{Na^{+1}/Na} = -2.714$ as reduction potential of silver is higher so it is less reactive while sodium having lower reduction potential is more reactive.
- (vi) Prediction of reaction of metals with dilute acids: Higher is the reduction potential of an acids low will be its tendency to lose electrons and lower will be its tendency to react with acids to liberate hydrogen and vice versa.
- (vii) Prediction of displacement of one metal by other: Metals lying above hydrogen in electrochemical series displace the metals lying below hydrogen in the electrochemical series, from aqueous soln of their salts e.g. Zn will displace Cu from CuSO₄ soln while Zn does not displace Mg from MgSO₄ soln.

Cell Reaction:

The cell reaction is obtained by the addition of two half reactions i.e. anode half reaction and cathode half reaction after equalizing gain and loss of electrons in the two half reactions e.g. for Daniel cell

Anode half reaction	$Zn \longrightarrow$	Zn^{+2} -	+ 2e⁻	(Oxidation)
Cathode half reaction	$Cu^{+2} + 2e^{-}$	\rightarrow	Cu	(Reduction)
Cell reaction	$Zn + Cu^{+2}$	\rightarrow	Zn^{+2}	+ Cu

Cell Representation:

A cell can be represented by line notation.

- Anode half is written on the left and cathode half on the right, the two are separated by a double vertical lines. The double vertical line also represents salt bridge.
- With in a half cell, reactants are written first and then products.
- A single vertical line separates two states (electrode and solution) in each half cell.
- Concentration of aqueous solution is written in parentheses after writing ion or molecule present in the solution.
- If some gas is also used in a cell, its pressure is mentioned in parentheses.
- e.g. (i) Daniell cell is written by line notation as $Zn\mid Zn^{+2}\left(1M\right)\mid\mid\quad Cu^{+2}\left(1M\right)\mid Cu$
- e.g. (ii) A cell consisting of hydrogen anode and copper cathode is written as $Pt / H_2 (1atm) \mid H^+ (1M) \parallel Cu^{+2} (1M) \mid Cu$
- e.g. (iii) A cell consisting of Zinc anode and hydrogen cathode is written as $Zn\mid Zn^{+2}\left(1M\right)\mid\mid H^{+}\left(1M\right)\mid H_{2}\left(1atm\right)/Pt$

Cell Voltage or e.m.f. of Cell:

The potential difference of anode and cathode that causes a flow of current from anode to cathode in the outer circuit is called cell voltage or e.m.f. of the cell. There are three methods of determining cell voltage.

(i) By difference of reduction potentials

Reduction potential of anode is subtracted from reduction potential of cathode.

$$E^{o}_{\text{Cell}} = E^{o}_{\text{Red (Cathode)}} - E^{o}_{\text{Red (Anode)}}$$

e.g. for Daniell Cell

$$E^{^{o}}{}_{^{Cell}} = E^{^{o}}{}_{^{Cu^{+2}}\!/^{Cu}} - E^{^{o}}{}_{^{Zn^{+2}}\!/^{Zn}} = 0.34 - (-0.76) = 0.34 + 0.76 = 1.10~V$$

(ii) By difference of oxidation potentials

Oxidation potential of cathode is subtracted from oxidation potential of anode.

$$E^{o}_{Cell} = E^{o}_{ox (anode)} - E^{o}_{ox (cathode)}$$

e.g. for Daniell Cell

$$E^{^{o}}{^{\text{Cell}}} = E^{^{o}}{^{\text{Zn'}}}{^{\text{Zn}^{+2}}} - E^{^{o}}{^{\text{Cu'}}}{^{\text{Cu}^{+2}}} = 0.76 - (-0.34) = 0.76 + 0.34 = 1.10 \ V$$

(iii) By summation of oxidation and reduction potentials:

Oxidation potential of anode is added to reduction potential of cathode.

$$E^{^{o}}{}_{\text{Cell}} = E^{^{o}}{}_{\text{ox (anode)}} \ + E^{^{o}}{}_{\text{Red (cathode)}}$$
 e.g. for Daniell Cell
$$E^{^{o}}{}_{\text{Cell}} = E^{^{o}}{}_{\text{Zn/Zn^{+2}}} + E^{^{o}}{}_{\text{Cu^{+2}/Cu}} = 0.76 + 0.34 = 1.10 \text{ V}$$

Electrical Cells:

The cells in which electrical energy is either produced or consumed are called electrical cells.

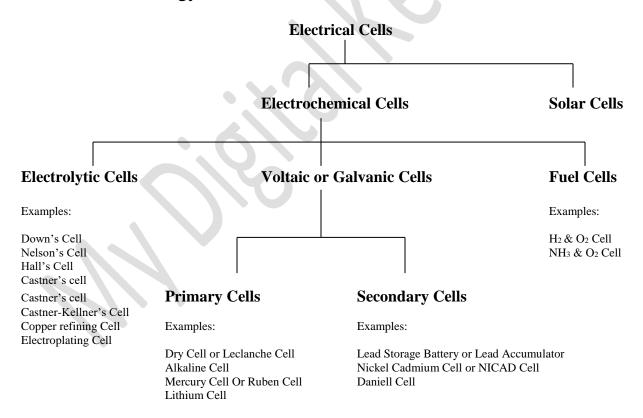
They are of two types:

(A) Electrochemical Cells:

In these cells inter-conversion of electrical and chemical energy take place.

(B) Solar Cells:

In these cells solar energy is converted into electrical energy.



(A) Electrochemical Cells:

"A device in which inter-conversion of electrical and chemical energy takes place is called electrochemical cell."

Classification of electrochemical cells:

Electrochemical Cells are divided into three types:

1. Electrolytic Cells:

The electrochemical cells in which electrical energy is converted to chemical energy are called electrolytic cells. They are non-spontaneous and their e.m.f is negative. Their process is endothermic. In these cells electrical energy is provided by external source and as a result chemical reaction occurs in the cell.

2. Voltaic or Galvanic Cells:

The electrochemical cells in which chemical energy is converted to electrical energy are called voltaic or galvanic cells. They are spontaneous and their e.m.f is positive. Their process is exothermic. In these cells chemical reaction occurs in the cell and electrical energy is produced which is provided to external user.

Voltaic or Galvanic cells are further divided into two types:

(a) Primary Cells:

The voltaic cells which can not be recharged are called primary cells.

(b) Secondary Cells:

The voltaic or galvanic cells which can be recharge are called secondary cells.

3. Fuel Cells:

The electrochemical cells in which a fuel gas and an oxidant is provided to the cell when it is under use and supply is cut down when the cell is to be stopped, are called fuel cells.

In H₂ & O₂ Cell, H₂ is fuel gas while O₂ is oxidant, similarly in NH₃ & O₂ Cell, NH₃ is fuel gas while O₂ is oxidant

Fuel cells are spontaneous and their e.m.f is positive. Their process is exothermic. In these cells chemical reaction occurs in the cell and electrical energy is produced which is provided to external user.

1. Electrolytic Cells:

A device which converts electrical energy into chemical energy is called electrolytic cell. In it electric current is used to drive a non-spontaneous reaction.

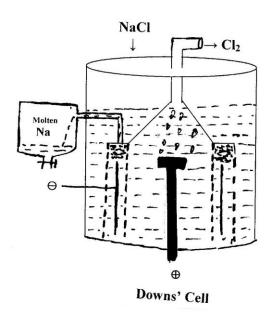
The process in which metals are obtained by the electrolysis of their molten or aqueous ores or salts in an electrolytic cell is called <u>electro-winning</u> of metals.

There are many electrolytic cells.

A few are following:

(i) **Downs' Cell**: (Electro-winning of Sodium)

Sodium was first extracted in 1807 by an English chemist Sir Humphrey Davy. He extracted sodium by electrolysis of molten sodium hydroxide. But now-a-day sodium is extracted by electrolysis of molten sodium chloride in Downs Cell.



The Cell is designed to collect molten sodium and chlorine separately with out allowing them to react with each other. Molten sodium chloride is taken in the cell. Melting point of NaCl is 800°C so to reduce M.P a mixture containing NaCl and CaCl₂ in molar ratio of 2:3 is taken which melts at $580^{\circ}\text{C} \approx 600^{\circ}\text{C}$.

Down cell was designed by J. C. Downs, it consists of a iron circular container through the bottom of which rises a graphite anode. The anode is surrounded by a circular iron cathode enclosed in a wire-gauze shell. Molten NaCl is taken in the cell. On electrolysis Cl⁻ ions move to anode where they oxidize to chlorine. The chlorine gas thus produced bubbles through molten NaCl into chlorine outlet. Na⁺ ions move towards iron cathode where they reduce to sodium metal.

	2NaCl _(s)	=	$2Na^{+}_{(1)} + 2Cl$	(1)
Reaction at anode	2Cl	\rightarrow	$Cl_2 + 2e^{-}$	(Oxidation)
Reaction at cathode	$2Na^{+} + 2e^{-}$	\rightarrow	2Na	(Reduction)
Overall reaction	2NaCl el	ectrolysis	$2Na + Cl_2$	

The molten sodium rises up through the pipe shown in fig and flows into receiver from which it is periodically drained out. Function of gauze is to prevent contact between two products so that they should not react.

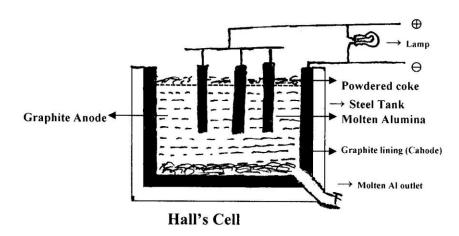
(ii) Castner's cell:

An other electrolytic cell is Castner's cell which is used to obtain sodium by the electrolysis of molten NaOH.

(iii) Hall's Cell: (Electro-winning of Aluminum)

It is used to obtain Aluminium from Alumina.

In 1886 Charles Martin Hall developed a process of obtaining Aluminum by electrolysis of molten alumina (Al₂O₃) dissolved in cryolite (Na₃AlF₆).



Aluminum is extracted from Bauxite Ore ($Al_2O_3.2H_2O$) in this cell. The ore contains impurities which are to be for this purpose.

(a) Baeyer's Process:

It is used to remove iron impurities. Crude ore is dissolved in 45% hot aqueous NaOH solution at 150°C. Ore is dissolves as sodium aluminate while ferric oxide separates out as red mud which is then filtered off.

$$Al_2O_3.2H_2O + 2 NaOH \rightarrow 2 NaAlO_2 + 3 H_2O$$

The solution is diluted with water and cooled to precipitate as aluminum oxide trihydrate. The $2 \text{ NaAlO}_2 + 4 \text{ H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3.3\text{H}_2\text{O} \downarrow + 2\text{NaOH}$ precipitate is filtered , washed and ignited in a rotary kiln at 1200°C to produce pure alumina.

$$Al_2O_3.3H_2O \rightarrow Al_2O_3 + 3H_2O$$

(b) Serpek's Process:

It is used to remove silica impurity. Powered ore is mixed with coke and heated to 1800°C in a current of nitrogen. Silica present in ore is converted to silicon vapours and carbon monoxide which are given off and aluminum nitride is left.

$$SiO_2 + 2C \rightarrow Si \uparrow + 2CO \uparrow$$

 $Al_2O_3.2H_2O + 3C + N_2 \rightarrow 2AlN + 3CO \uparrow + 2H_2O \uparrow$

The aluminum nitride then on hydrolysis changes to aluminum hydroxide which then heating changes to alumina.

$$AlN + 3H_2O \rightarrow Al(OH)_3 + 3NH_3 \uparrow$$

 $Al(OH)_3 = 1200^{\circ}C \rightarrow Al_2O_3 + 3H_2O \uparrow$

Electrolysis of Alumina (Hall's Process):

Pure alumina has high melting point and is non conductor even in molten state hence it is dissolved in cryolite (Na₃AlF₆)and the mixture is melted at 960-980°C lower than that of pure alumina. The electrolyte is taken in the electrolytic cell which consists of steel tank lined inside with graphite which serves as cathode. Graphite rods which serve as anode are suspended in molten electrolyte. A current of 6-7 volts and 100 amperes is passed through molten electrolyte. Heat produced by current keeps the mass in fused state. As a result of electrolysis following reactions occur

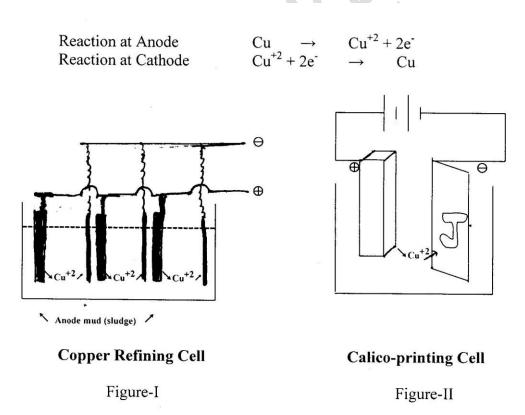
The aluminum produced at cathode sinks to bottom from where it is drained out, while atomic oxygen produced at anode reacts with powdered coke dusted on the molten alumina so the graphite anode will be protected. Concentration of alumina falls as a result of electrolysis so resistance of bath increases. When the resistance increases to certain limit the charge control lamp will light up and then more alumina will then be added.

(iv) Anodizing of Aluminum:

Anodized aluminum is prepared by making it anode in an electrolytic cell containing sulphuric acid or chromic acid, which coats a thin layer of oxide on it. The aluminium oxide layer protects aluminium from corrosion. The freshly anodized aluminium is hydrated and can absorb dyes.

Refining of Copper:

Blistered copper obtained by reduction of chalcopyrite is not much pure and is not good conductor so electrolytic refining of copper is carried out to get 99.9% pure copper, which is a good conductor. Large slabs of blistered copper are made anode while thin sheets of pure copper are made cathode and these are dipped in copper sulphate solution. On electrolysis blistered copper dissolves by oxidizing to Cu⁺² ions, the ions move to cathode where they reduce to copper and get deposited on cathode. As anode dissolves so it becomes thin while cathode grows due to deposit of copper on it. The impurities like silver, gold and platinum settle down as anode mud (or sludge). See Figure-I shown below.



(vi) **Electroplating**:

Copper, Silver, Nickel or Chromium plating is done by various types of electrolytic cells. The metal to be coated is made as anode while the metal on which coating is to be done is made as cathode. The two electrodes are dipped in the solution having cations of anode. A slat bridge is also used.

(vii) Calico-printing:

To write on a metal sheet with metal using a stencil is called calico-printing. The cell used for this purpose is shown in Figure-II given above.

A copper sheet is made cathode, while a copper bar is made anode. The copper cathode will be covered with wax paper stencil that has cut writing on it. The area under cutting is exposed so Cu⁺² ions approach here and reduced to copper and will be deposited on copper sheet on this exposed area. Thus required word will be printed on the cathode sheet.

(viii) Nelson Cell:

Nelson Cell is an electrolytic cell used to electrolysis of Brine (conc aq NaCl soln) to obtain Caustic Soda (NaOH), where Cl₂ and H₂ are obtained as by products. Nelson cell consists of perforated steel vessel (See Figuer-I and Figure-III shown below). It is lined inside with asbestos. The steel vessel act as container as well as cathode.

It is suspended in outer tank. Brine is taken in steel vessel and graphite or titanium anode

is dipped in the brine. On passing electric current, the Cl $^-$ ions move to anode and oxidize to chlorine gas which is given off through an out let and is collected in cylinders. Na $^+$ ions & H₂O molecules comes out of asbestos lining. On contact with steel cathode Na $^+$ ions reduce to sodium which on reaction with water produce sodium hydroxide which falls in catch basin placed on the bottom of outer tank where as hydrogen gas produced is expelled through outlet and is filled in cylinders.

$$2NaCl \implies 2Na^+_{(aq)} + 2Cl^-_{(aq)}$$
 Reaction at anode Reaction at cathode
$$2Cl^-_{(aq)} \rightarrow Cl_2 + 2e^- \quad \text{(Oxidation)}$$

$$2Na^+_{(aq)} + 2e^- \rightarrow 2Na \quad \text{(Reduction)}$$

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$$

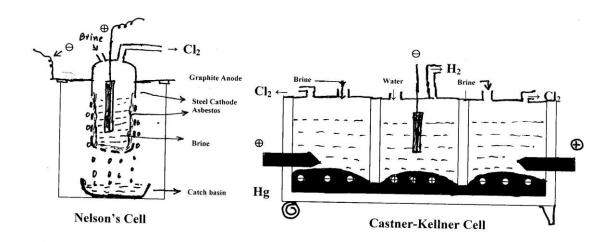


Figure-II

Cl₂ gas

Molten NaCl
and CaCl₂

Molten Na

Cylindrical steel cathode $2 \text{ Na}^+(l) + 2 \text{ e}^- \rightarrow 2 \text{ Na}(l)$ Graphite anode $2 \text{ Cl}^-(g) + 2 \text{ e}^-$

Nelson's Cell Figure-III

(ix) Castner-Kellner Cell:

Castner-Kellner Cell is used for electrolysis of Brine to obtain caustic soda (NaOH) with Cl₂ & H₂ as by products. See Figure-II shown above.

2. Voltaic or Galvanic Cells:

The cell in which chemical energy is converted into electrical energy by spontaneous redox reaction is called Voltaic or Galvanic cell.

In 1791, an Italian Professor of anatomy named Luigi Galvani noticed that the leg muscles of freshly dissected frog contracted when they were connected to one of the frog's nerves with a circuit composed of two metals. From this, another Italian professor of physics, Alessandro Volta, gave the idea that the frog's leg was a detector of the electric current generated by the bimetallic circuit. As on the basis of their work idea of this cell was obtained, so in recognition to their work the cell is given the name as voltaic or galvanic cell.

A voltaic cell consists of two half cells i.e. anode half and cathode half, oxidation occurs in anode half while reduction occurs in cathode half reaction. A typical example of voltaic cell is.

Daniell Cell:

In it anode is zinc rod dipped in 1M ZnSO₄ solution, in this half following equilibrium is established:

$$Zn = Zn^{+2} + 2e^{-}$$

Zinc oxidizes to zinc ions and electrons are gathered with zinc rod due to which electric potential develops on electrode.

Similarly in cathode copper rod dipped in 1M CuSO₄ solution, following equilibrium is established in this half cell:

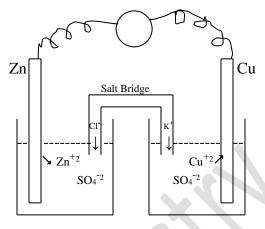
$$Cu \rightleftharpoons Cu^{+2} + 2e^{-}$$

Copper oxidizes to copper ions and electrons are gathered with copper rod due to which electric potential develops on electrode. But copper has low tendency to be oxidized than zinc so less potential will develop on it. When two electrodes are connected by wire, electrons flow from zinc electrode (anode) to copper electrode (cathode) in the outer circuit. Zinc will further oxidize to zinc ions again to met with deficiency of electrons occurred on it, where as copper will give extra electrons to copper ions which will deposit on it. Following reactions will now take place in the cell.

Reaction at anode $Zn \rightarrow Zn^{+2} + 2e^{-}$ (Oxidation)

Reaction at cathode $Cu^{+2} + 2e^{-} \rightarrow Cu$ (Reduction)

As a result of this redox reaction the cell will give a study current. But now the two solutions will not electrically neutral. The Solution in anode compartment become +ve while in cathode compartment becomes –ve. It will stop the working of cell. So salt bridge will be used to keep the two solutions neutral. A salt bridge is a glass tube containing saturated solution of a soluble salt like KCl in gel. It sends Cl ions to anode compartment



Daniell Cell

to balance Zn⁺² and K⁺ ions will be sent to cathode compartment to replace Cu⁺² ions so the two solutions remain electrically neutral and the cell will work longer.

Cell Reaction of Daniell Cell:

The cell reaction is obtained by the addition of two half reactions i.e. anode half reaction and cathode half reaction. e.g. for Daniel cell

Anode half reaction $Zn \rightarrow Zn^{+2} + 2e^{-}$ (Oxidation)

Cathode half reaction $Cu^{+2} + 2e^{-} \rightarrow Cu$ (Reduction)

Cell reaction $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

Cell Representation of Daniell Cell:

e.g. (i) Daniel cell is written by line notation as

$$Zn | Zn^{+2} (1M) | Cu^{+2} (1M) | Cu$$

Cell Voltage or e.m.f. of Daniell Cell:

(i) By difference of reduction potentials

Reduction potential of anode is subtracted from reduction potential of cathode.

$$E^{^{o}}{}_{^{Cell}} = E^{^{o}}{}_{^{Cu^{+2}}/^{Cu}} - E^{^{o}}{}_{^{Zn^{+2}/^{}}/^{Zn}} = 0.34 - (-0.76) = 0.34 + 0.76 = 1.10 \ V$$

(iii) By difference of oxidation potentials

Oxidation potential of cathode is subtracted from oxidation potential of anode.

$$E^{^{o}}_{^{\; Cell}} = E^{^{o}}_{^{\; Zn/Zn^{+2}}} - E^{^{o}}_{^{\; Cu/}} c_{u^{+2}} = 0.76 - (-0.34) = 0.76 + 0.34 = 1.10 \text{ V}$$

(iv) By summation of oxidation and reduction potentials:

Oxidation potential of anode is added to reduction potential of cathode.

$$E^{o}_{cell} = E^{o}_{z_{n}/z_{n}^{+2}} + E^{o}_{cu^{+2}/cu} = 0.76 + 0.34 = 1.10 \text{ V}$$

Types of Voltaic or Galvanic cells:

The Voltaic or Galvanic Cells are further divided into two categories i.e. primary cells and secondary cells.

(I) **Primary Cells:**

The voltaic or galvanic cells which are not rechargeable are called primary cells.

(i) **Dry Cell or Leclanche Cell:**

This cell was designed by Leclanche in 1887. The cell consists of Zinc can or cup that acts as anode. The can is lined inside by porous paper or cloth which prevents the direct contact of zinc with other reactants but permits the ions to pass through it. In the centre there is graphite rod which acts as cathode. The rod is surrounded by mixture of manganese dioxide (MnO₂) and powdered carbon. This mixture is contained in muslin bag which is surrounded by paste of starch and ammonium chloride (NH₄Cl). Some zinc chloride is also added to improve the conductivity. Following reactions occur in the cell.

At anode
$$Zn \rightarrow Zn^{+2} + 2e^{-}$$

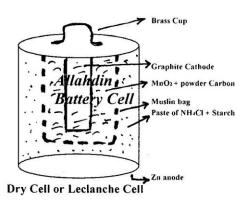
At cathode
$$2NH_4^+ + 2e^- \rightarrow 2NH_3 + H_2$$

The hydrogen thus produced reacts with manganese dioxide to produce dimanganese trioxide $2MnO_2 + H_2 \rightarrow Mn_2O_3 + H_2O$

The ammonia formed will react with zinc ions and produce tetra ammine zinc ions. $Zn^{+2} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{+2}$

This reaction prevents the increase in conc of Zn^{+2} ions and thus keeps the potential of zinc electrode constant.

Dry cell has a potential difference of 1.5 V.



(ii) Alkaline Cell:

The first dry alkaline cell was prepared in 1947. In this cell Zinc rod acts as anode while MnO₂ act as cathode. The electrolyte is KOH and hence it is called alkaline cell. The cell is enclosed in steel container. Zinc rod is made porous to give larger effective area. This cell give more current than common dry cell and has longer life.

At anode $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

At cathode $2MnO_2 + 2H_2O + 2e^- \rightarrow 2MnO(OH) 2OH^-$

Potential difference of the cell is 1.25 V.

(iii) Mercury Cell Or Ruben Cell:

This cell was developed in 1947. During discharging its potential does not drop significantly so it gives constant current so it is used in sensitive instruments. However it is expensive. Its voltage is 1.344 V. Its cell representation is

 $Zn \mid KOH, ZnO \parallel H_2O \mid HgO, Hg$

(iv) **Lithium Cell**:

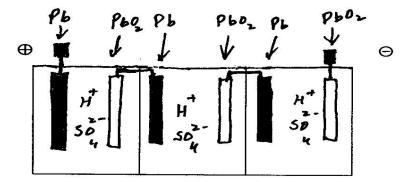
It is a long life and small size cell. It gives low power. It is used in Cameras, Heart pacemakers, electronic wrist watches etc.

(II) <u>Secondary Cells</u>:

The voltaic or galvanic cells which are rechargeable are called secondary cells.

(i) Lead Storage Battery or Lead Accumulator:

It is a battery normally used in automobiles. In it a group of secondary cells is connected in series. Each individual cell is of 2 volts so a 12V battery consists of 6 cells and a 6V battery consists of 3 cells. At start it provides a current of about 300A for short time but then 25A for over 2 hours. It consists of a plastic case divided into compartments, each compartment acts as a cell of 2V. In these cells 30% H₂SO₄ solution (Density 1.25 g/cm³) is present. Lead plate acting as anode and lead dioxide acting as cathode are dipped in this solution. Anode of one cell is connected to cathode of other cell. When the battery is used to start the car, it acts as voltaic cell as it supply electrical energy but then generator of car starts and it now supply electrical energy to the battery and the battery now becomes electrolytic cell and is recharged now.



Lead Storage Battery or Lead Accumulator

Following are the reactions occur in the cell.

Reactions during discharging:

At anode $Pb \rightarrow Pb^{+2} + 2e^{-}$

$$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$$

The lead sulphate being insoluble gets deposited on lead plate.

At cathode $PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{+2} + 2H_2O$

 $Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$

The lead sulphate being insoluble gets deposited on lead oxide plate also. When density of sulphuric acid drops to 1.15 g/cm³ the cell stops working

Reactions during recharging:

To charge the battery it is connected to external source which supply higher voltage than that of battery. The lead sulphate coating on lead plate is converted back to lead

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{-2}$$

On the other electrode lead dioxide and sulphuric acid is reproduced.

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{-2} + 2e^-$$

Density of sulphuric acid again increases.

(ii) Nickel Cadmium Cell or NICAD Cell:

It is another secondary cell as it can be recharged. The anode is cadmium, while cathode is Nickel oxide while electrolyte is alkaline solution.

Reactions during discharging are:

At anode $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

At cathode $NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$

Reverse reactions occur during charging.

The cell voltage is 1.4 V. These cells undergo self discharge within a few months so they are not suitable for intermittent (occasional) use.

(iii) **Daniel Cell:**

It is also secondary cell as it can be recharged.

3. **Fuel Cells**:

The electrochemical cell in which a combustion reaction is used to generate electrical energy is called fuel cell. In fuel cells reactants are continually supplied

and products are continually removed. They work as long as fuel is provided to them. These cells are used in space vehicles. e.g Hydrogen-Oxygen fuel cell. It is shown in figure. Porous Platinum Electrodes are used in it. Electrolyte is KOH.

Following reaction take place:

At anode $2H_2 \rightarrow 4H^+ + 4e^-$

 $4 \text{ H}^+ + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O}$

Hydrogen-oxygen Fuel Cell

At cathode $O_2 + 4e^- \rightarrow 2O^{-2}$

 $20^{-2} + 2H_2O \rightarrow 4OH^{-1}$

Overall Cell Reaction $2H_2 + O_2 \rightarrow 2H_2O$ $E^{\circ}_{Cell} = 1.10 \text{ V}$

Water produced in the reaction is in vapour state, it is condensed and is used by astronaut for drinking purpose. Beside hydrogen, ammonia and hydrazine (N_2H_4) are also used in fuel cells.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \ E^{\circ}_{Cell} = 1.17 \ V$$

There are many other fuel cells.

Applications of Batteries & Fuel Cells:

- Pb/acid cell is used in automobiles.
- In Electrically Powered Vehicles (ECV's), batteries are used and they replace combustion engine.
- Ni-Cd cell, NiMH and lithium ion cell are secondary cells and they are used in portable high power applications such as computers, power tools, flash lights, and medical devices.
- Lithium cell is primary cell and it is used in portable low power applications such as cameras, wrist watches, calculators, heart pacemaker etc.

- Primary cells are used in missile guidance and communication devices.
- Mercury, silver oxide batteries are used in hearing aids.
- Fuel cells are used as power source in buses, boats, trains, aeroplanes etc.
- Miniature (micro) fuel cells are used in cellular phones, laptops, and portable electronics, pagers, video recorders, smoke detectors, burglar alarms, hotel locks etc.
- Fuel cells are used in hospitals, credit card centre, police stations and banks.
- Wastewater treatment plants produce methane which is converted by fuel cells to electricity.

Corrosion:

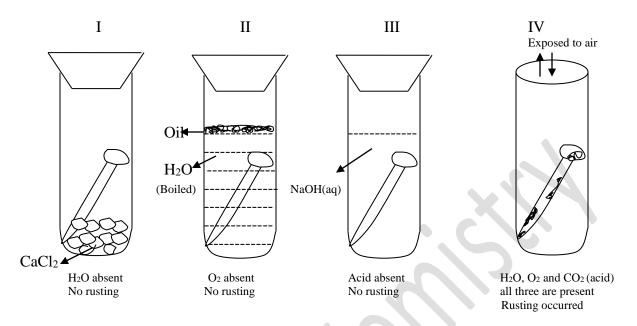
The slow eating away of a metal due to action of environment is called corrosion. If pure iron is exposed to moist air it get corroded and converted to reddish brown mass known as rust. Rust is a hydrated oxide i.e. hydrated iron(III)oxide {2Fe(OH)₃ or Fe₂O₃.3H₂O}.

There are two theories about corrosion.

(i) Acid Theory:

According to this theory three things are compulsory i.e. oxygen, water and acid, for corrosion. If any one of them is missing no rusting will occur and it can be experimentally verified.

- If iron nail is placed in test tube containing calcium chloride (solid) it will not get rusted. It is due to the reason that CaCl_{2(s)} (a hygroscopic substance) present in the test tube absorbed moisture and in absence of water no corrosion occurred.
- If iron nail is placed in test tube containing water that is boiled for longer time and is covered with an oil layer, it will not get rusted as in this case dissolved oxygen is removed by longer time boiling so no corrosion occurred.
- If iron nail is placed in NaOH solution it will not get rusted as no acid is there.



• In first three test tubes iron nails are not rusted as one or the other component in each test tube is missing while in fourth test tube the nail is rusted as all the three components are present.

In moist air iron gets rusted as in moist air water (water vapour), oxygen and acid (CO₂ is acidic gas) are there which cause rusting of iron.

Following reactions occur:

Fe + 2CO₂ + H₂O +
$$\frac{1}{2}$$
O₂ \rightarrow Fe (HCO₃)₂
2Fe(HCO₃)₂ + [O] \rightarrow 2Fe (OH)CO₃
2Fe (OH)CO₃ \rightarrow 2Fe(OH)₃ + 2CO₂

(ii) Electrochemical theory:

According to this theory, rusting is an oxidation-reduction reaction. During rusting non-uniform surface of iron act as an electrolytic cell. One portion becomes anode and other cathode. Oxidation occurs at anode part and as a result Fe^{+2} ions are produced. The ferrous ion further oxidizes by oxygen to ferric (Fe^{+3}) ion. The electrons lost during oxidation, travel along surface

$$2\text{Fe} \rightarrow 2\text{Fe}^{+2} + 4\text{e}^{-}$$

 $2\text{Fe}^{+2} \rightarrow 2\text{Fe}^{+3} + 2\text{e}^{-}$

of metal to cathode. At cathode oxygen gains electrons and reduces, then it reacts with water and produce hydroxyl ions.

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

Fe⁺³ and OH ions form rust.

$$2\text{Fe}^{+3} + 6\text{OH}^{-} \rightarrow 2\text{Fe}(\text{OH})_3$$
 or $\text{Fe}_2\text{O}_3.3\text{H}_2\text{O}$

The rust mass is porous thus air passes through pores and cause further rusting of iron and ultimately whole iron get rusted.

$$Fe^{3+} \rightarrow Fe(OH)_3 \leftarrow OH^*$$

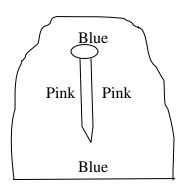
$$-e^* \quad Rust$$

$$2Fe \rightarrow Fe^{2+} + 2e^* \qquad 2H_2O + O_2 + 4e^* \rightarrow 4OH^*$$

$$+ \quad Iron \ rod \qquad -$$

Experiment:

We can verify electrochemical theory experimentally. If potassium ferricyanide, phenolphthalein and agar powder is added to water and then after boiling and cooling the solution, a transparent gel is obtained. If an iron nail is pushed in the jelly and left for few hours, blue colour will appear near head and tip of the nail and at same time pink colour is developed along the body of the nail.



Colourless gel

Appearance blue colour indicates the presence of ferrous ions.

$$Fe^{+2} + K_3[Fe(CN)_6] \longrightarrow KFe[Fe(CN)_6] + 2K^+$$
Potassium ferricyanide Potassium ferriferrocyanide (Blue)

Where as appearance of pink colour indicates presence of OH ions. Colourless phenolphthalein turns pink in basic medium (OH).

• If iron is contact with metals which have more reduction potential than iron e.g. Cu, Sn etc, then its rusting speeds up. But if iron is in contact with metals whose reduction potential is less than iron e.g. Zn, Mg etc, then it is protected from corrosion. In other words when iron comes in contact with less active metals (lower in electrochemical series) e.g. Cu, Sn etc a galvanic cell is establish in which iron releases electrons and forms cation thus corrosion speeds up. But if iron is in contact with more active metals (higher in electrochemical series) e.g. Zn, Mg etc a galvanic cell is establish in which active metals releases electrons and iron receive electrons forming anion thus it will be protected from corrosion.

Prevention of corrosion:

Various methods are applied to prevent corrosion. A few are following.

(j) By coating:

Coating of iron with paint, enamel, grease, oil etc iron is protected from corrosion.

(iii) By electroplating

Electroplating of iron with Nickel, Chromium etc iron is protected from corrosion.

(iii) **By tinning:** When clean sheet of iron is dipped in bath of molten tin (M.P=230°C) and then passing it through hot pair of rollers, a uniform layer of tin is coated on iron and protects it from corrosion as long as its layer on iron is intact. But if this layer is damaged then iron comes into contact with moisture. A galvanic cell is established in which tin act as cathode and iron as anode. Electrons flow from iron to tin. Iron cations form Fe(OH)₃

(rust) with OH of water. Thus coated iron with tin get rusted more rapidly when tin layer is damaged than the non-coated iron.

(iv) **By galvanizing**:

Coating of zinc on iron to protect it from corrosion is called galvanizing. Iron is cleaned by dipping in acid bath (pickling). It removes oxide from it. Then zinc coating is carried out by one of the following methods.

(a) By dipping: Iron sheets are dipped in molten zinc (M.P = 419°C) and then passed through hot pair of rollers. A uniform layer of zinc is coated on iron.

- (b) By electroplating: When iron is made cathode and is dipped in zinc sulphate
- (c) By sherardizing: In this method zinc dust is vapourized by heating it strongly and then vapours are allowed to condense on iron surface. Iron get coated with zinc.

(v) **By dipping**:

The iron in orthophosphoric acid bath, a tenacious (which does not easily remove) layer of iron phosphate is produced which protects iron from corrosion.

(v) Sacrificial protection or cathodic protection:

When iron remains in contact with metals which are better reducing agent than iron e.g. Zn, Mg etc, it is protected from corrosion.

Iron forms galvanic cell with Zn or Mg, in the cell, iron act as cathode and Zn or Mg act as anode. Thus Zn or Mg oxidize to cations and iron is protected. This is called cathodic or sacrificial protection.

(viii) Removal of strains:

The mechanical strains act as centres of corrosion. If these strains are removed further corrosion stops.

(ix) By Alloying the Iron with other metals:

If iron is converted to stainless steel (an alloy of iron) it is protected from corrosion. Stainless steel beside iron contains 8% nickel, 18% chromium and 0.18% carbon.