By- SHAILENDRA SHUKLA SIR

Electrochemical Cell

It is a device which converts chemical energy into electrical energy. Here, a redox reaction is carried out in indirect manner and decrease in free energy during the reaction is observed as electrical energy.

Let us consider a simple electrochemical cell consisting of zinc and copper electrodes. Here, a zinc rod remains dipped in aqueous solution of zinc sulphate while, a copper rod remains dipped in aqueous solution of copper sulphate. Both of these two rods remain connected together through voltmeter and both the solutions remain chemically connected using salt bridge.

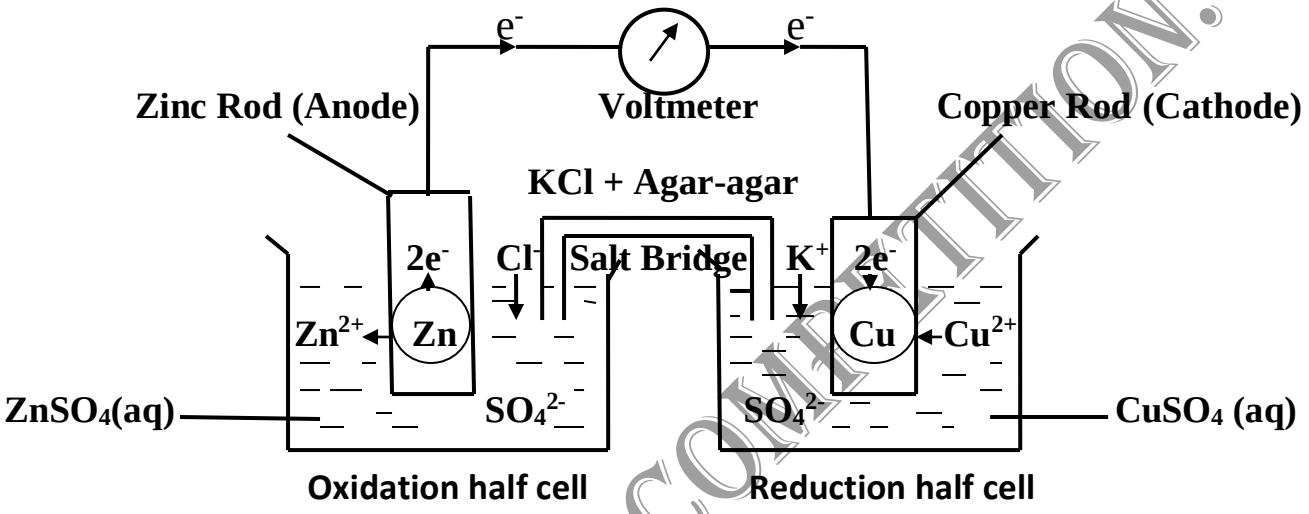


Fig. – Electrochemical Cell

During cell operation, zinc atoms of zinc rod lose their valence electrons on rod and come into solution as $Zn^{2+}(aq)$ ions. These electrons move towards copper rod through conducting wires where, they are taken by $Cu^{2+}(aq)$ ions of solution. Thus, the electrode reactions and over all cell reaction occurring in cell will be as under-

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

At cathode $Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s)$ (reduction half reaction)

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

(Complete cell reaction)

Here, oxidation occurs at zinc electrode and therefore, it acts like anode, while reduction occurs at copper electrode and therefore, it acts like cathode. Furthermore, since the electrons are released on anode, it is negatively charged while, they are taken from cathode, it is positively charged. Thus, in electrochemical cells the anode is negatively charged while, the cathode is positively charged.

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Here, due to flow of electrons from the anode to the cathode electricity is generated, which flows in the direction opposite to the direction of flow of electrons i.e. from the cathode to the anode.

Salt Bridge and its Function

It is an inverted U-tube consisting of glass and remains filled with a semi-solid paste of an inert electrolyte such as KCl, KNO_3, $NaNO_3$, NH_4Cl etc with agar-agar. Its one end remains dipped in anodic solution, while another end in cathodic solution. Both of these two ends remain provided with cotton plug to provide mechanical support to the paste.

Functions of Salt Bridge

Salt bridge performs following two important functions in an electrochemical cell-

(1) It complete the circuit by providing chemical contact to the anodic and cathodic solutions, so that, the flow of electrons occurs continuously in the cell and therefore, electricity is generated continuously.

(2) It maintains electrical neutrality of anodic and cathodic solutions by furnishing appropriate number of anions and cations in these solutions, so that flow of electrons occurs continuously in the cell and therefore, electricity is generated continuously.

If salt bridge is not used, then after some time, anodic solution will become positively charged and cathodic solution will become negatively charged. Hence, the flow of electrons will obstructed and generation of electricity will get stopped.

Symbolic Representation of Electrochemical Cell

Following are international conventions for the symbolic representation of an electrochemical cell-

(1) Anode is always represented on left hand side while, the cathode is represented on right hand side.

(2) During representation of anode metal is represented first and it is followed by metal ion. Both of these two are separated either by semi colon or by single vertical line.

$$M(s) \mid M^{n+}(aq)$$

Anode

For example, zinc electrode acting like anode can be represented as under-

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

Anode

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(3) During representation of cathode metal ion is represented first and it is followed by metal. Both of these two are separated either by semi colon or by single vertical line.

$$M^{n+}(aq) \mid M(s)$$

Cathode

For example, copper electrode acting like cathode can be represented as under-

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

Cathode

(4) Both anode and cathode are separated by two parallel vertical lines which represents the salt bridge.

(5) Some time, molar concentration of electrolytes is also represented in parentheses after the symbol of metal ion.

For example, zinc-copper cell involving following cell reaction-

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

can be symbolically represented as under-

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

Anode Salt bridge Cathode

Q.- Give the symbolic representation of an electrochemical cell involving following cell reaction-

$$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

Ans.- Here, copper electrode is acting like anode, while, silver electrode is acting like cathode. Hence, the electrochemical cell involving given cell reaction can be symbolically represented as under-

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

Anode Salt bridge Cathode

Q.- Give the electrode reactions and the complete cell reaction occurring in following electrochemical cell-

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

Ans.- In given electrochemical cell, copper electrode is acting like anode, while silver electrode is acting like cathode. Hence, the electrode reactions and the complete cell reaction occurring in this electrochemical cell can be represented as under-

At anode- $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ (oxidation half reaction)

At cathode $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$ (reduction half reaction)

$$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

(complete cell reaction)

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Electrode Potential

If a metal rod is dipped in aqueous solution of its salt, then after some times the rod becomes either positively or negatively charged with respect to the solution. Thus, a charge difference (potential difference) gets developed between metal rod and solution. This potential difference is called electrode potential of the respective electrode.

For example, if a zinc rod is dipped in aqueous solution of $ZnSO_4$, then after some times the rod becomes negatively charged with respect to the solution i.e. a negative electrode potential gets developed on zinc electrode.

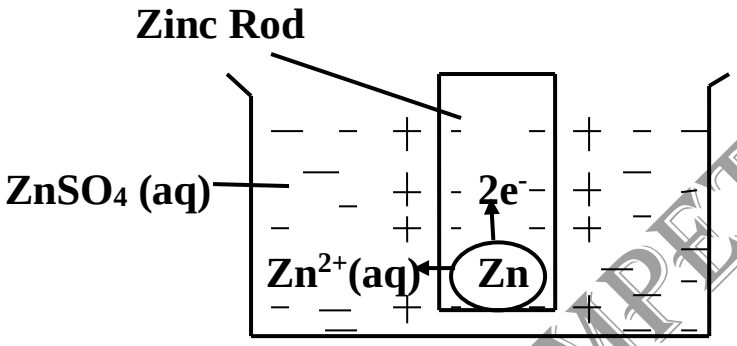


Fig.- Development of negative electrode potential on zinc electrode

Similarly, if a copper rod is dipped in aqueous solution of $CuSO_4$, then after some times the rod becomes positively charged with respect to the solution i.e. a positive electrode potential gets developed on copper electrode.

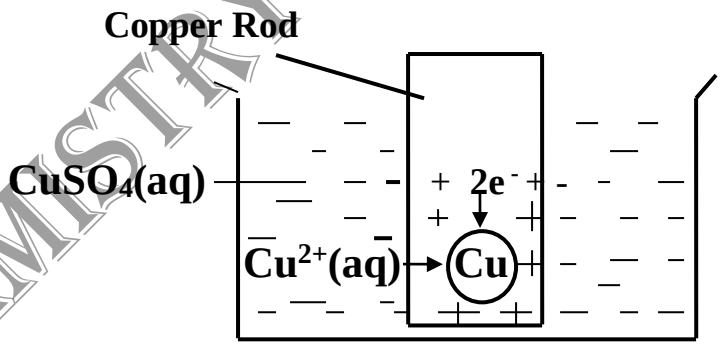


Fig.- Development of positive electrode potential on copper electrode

In fact, if a metal rod is dipped in aqueous solution of its salt, following two important cases may arise-

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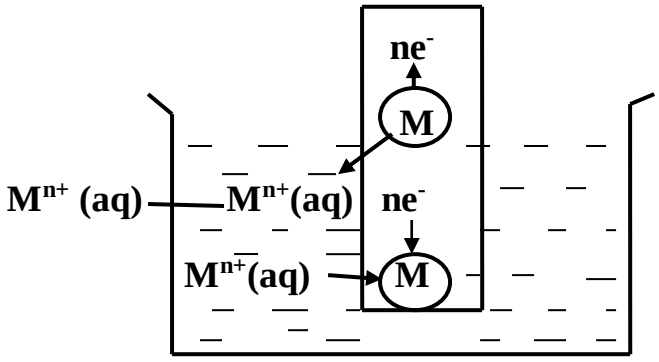


Fig. – Development of electrode electrode potential

(1) Metal atoms of metal rod lose their electrons on rod and come into solution as metal ions.

$$M\ (s) \rightleftharpoons M^{n+} + ne^-$$

This reaction is reversible, where at equilibrium the metal rod is negatively charged due to presence of excess of electrons. Thus, a negative electrode potential gets developed on metal rod. For example, zinc electrode.

(2) Metal ions of solution take electrons from rod and get reduced into metal atoms. These metal atoms either get deposited on metal rod or get settled on the bottom.

$$M^{n+} + ne^- \rightleftharpoons M\ (s)$$

This reaction is reversible, where at equilibrium the metal rod is positively charged due to deficiency of electrons. Thus, a positive electrode potential gets developed on metal rod. For example, copper electrode.

Types of Electrode Potential

Electrode potential may be of following two types-

(1) Oxidation Potential

The tendency of an electrodes to get oxidized i.e. to give electrons is called is called oxidation electrode potential of the electrode. For example,

$$M\ (s) \rightleftharpoons M^{n+} + ne^-$$
$$Zn\ (s) \rightleftharpoons Zn^{2+} + 2e^-$$
$$\tfrac{1}{2}\ H_2\ (g) \rightleftharpoons H^+ + e^-$$

Oxidation electrode potential is the measure of capacity of the electrode to get oxidized. The larger the value of oxidation electrode potential, more is capacity of the electrode to get oxidized.

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(2) Reduction Potential

The tendency of an electrodes to get reduced i.e. to take electrons is called is called reduction electrode potential of the electrode. For example,

$$M^{n+} + ne^- \rightleftharpoons M\ (s)$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu\ (s)$$
$$H^+ + e^- \rightleftharpoons \tfrac{1}{2} H_2\ (g)$$

Reduction electrode potential is the measure of capacity of the electrode to get reduced. The larger the value of reduction electrode potential, more is capacity of the electrode to get reduced.

All the electrodes have both oxidation and reduction electrode potentials. The numerical values of these two electrode potentials are also same for an electrode but they have opposite sign. Thus,

$$E_{oxidation} = - E_{reduction}$$

For example, standard oxidation electrode potential of zinc electrode is +0.76V, hence its standard reduction electrode potential will be –0.76V. Similarly, standard oxidation electrode potential of copper electrode is -0.34 V, hence its standard reduction electrode potential will be +0.34 V.

Following Europian convention, in India, standard reduction potential is taken as standard electrode potential of the electrode.

Standard Hydrogen Electrode (SHE)

It is a primary standard reference electrode, which is used to measure relative standard electrode potential of different electrode. It contains a platinum wire fused in a thin glass tube and is remains fitted with a platinum foil coated with platinum black. Thin glass tube remains jacketed with a hard glass jacket having opening for passing hydrogen gas. The platinum foil remains dipped in 1M HCl solution in such a way that its two-third part remains dipped in solution, while one-third remains exposed to hydrogen gas being constantly bubbled in solution at 298 K temperature and 1 atm pressure.

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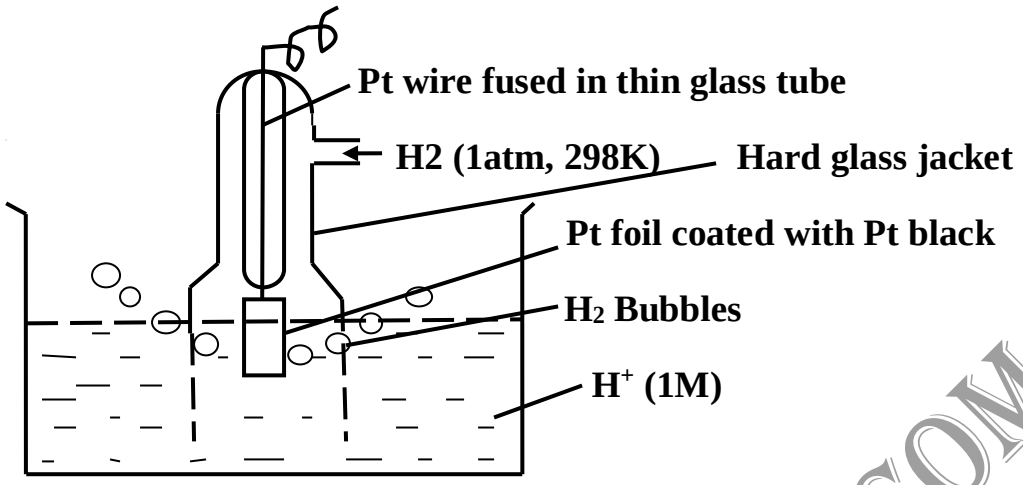


Fig.- Standard Hydrogen Electrode (SHE)

SHE is a primary standard reversible electrode, which can act both like anode and cathode.

(a) When SHE acts like anode, then oxidation occurs on this electrode.

$$\frac{1}{2} H_2 \rightleftharpoons H^+ + e^- \quad \text{(oxidation)}$$

Here, this electrode is represented as under-

$$Pt, H_2(1atm) \mid H^+(1M)$$

Anode

(b) When SHE acts like cathode, then reduction occurs on this electrode.

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2 \quad \text{(reduction)}$$

Here, the electrode is represented as under-

$$H^+(1M) \mid H_2(1atm), Pt$$

Cathode

The standard electrode potential of SHE has been arbitrarily fixed to be $\pm$ 0.00 V and that of other electrodes is determined with respect to this electrode.

Determination of Standard electrode potential

For experimental determination of Standard electrode potential of an electrode, the electrode in standard conditions (298 K, 1 atm) is connected to SHE to make an electrochemical cell and its standard cell potential is determined. Now knowing the standard cell potential (E^0_{cell}) and standard electrode potential of one of the electrodes, that of another electrode can be calculated using following formula-

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

For example, let we have to determine the standard electrode potential of zinc electrode. Here, zinc electrode in standard conditions is connected with SHE through a voltmeter to make an electrochemical cell. Here, the direction of flow of electrons is from zinc electrode to SHE, which indicates that, zinc electrode is

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acting like anode and SHE is acting like cathode. Hence, electrode reactions and overall cell reaction occurring in cell will be as follows-

At anode- $Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^-$ (oxidation half reaction)
At cathode $2H^+\,(aq) + 2e^- \rightarrow H_2\,(g)$ (reduction half reaction)

$$Zn(s) + 2H^+\,(aq) \rightleftharpoons Zn^{2+}(aq) + H_2\,(g)$$

(complete cell reaction)

The cell representation of this electrochemical cell will be as under-

$$Zn(s) \mid Zn^{2+}(aq) \parallel 2H^+\,(aq) \mid H_2\,(g), Pt$$

Here, from voltmeter, standard cell potential of the cell,

$E^0_{cell} = 0.76\ V$

$\therefore \quad E^0_{cell} = E^0_{H^+/H2} - E^0_{Zn^{2+}/Zn}$

or $\quad 0.76\ V = 0.00V - E^0_{Zn^{2+}/Zn}$

or $\quad E^0_{Zn^{2+}/Zn} = -\,o.76\ V$

Thus, standard electrode potential of zinc electrode is - o.76 V.

Similarly, let we have to determine the standard electrode potential of copper electrode. Here, copper electrode in standard conditions is connected with SHE through a voltmeter to make an electrochemical cell. Here, the direction of flow of electrons is from SHE to copper electrode, which indicates that, SHE is acting like anode and copper electrode is acting like cathode. Hence, electrode reactions and overall cell reaction occurring in cell will be as under-

At anode- $H_2\,(g) \rightarrow 2H^+\,(aq) + 2e^-$ (oxidation half reaction)
At cathode $Cu^{2+}\,(aq) + 2e^- \rightarrow Cu(s)$ (reduction half reaction)

$$H_2\,(g) + Cu^{2+}\,(aq) \rightleftharpoons 2H^+\,(aq) + Cu(s)$$

(complete cell reaction)

The cell representation of this electrochemical cell will be as under-

$$Pt, H_2\,(g) \mid H^+(aq) \parallel Cu^{2+}\,(aq) \mid Cu(s)$$

Here, from voltmeter, standard cell potential of the cell,

$E^0_{cell} = 0.34\ V$

$\therefore \quad E^0_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{SHE}$

or $\quad 0.34\ V = E^0_{Cu^{2+}/Cu} - 0$

or $\quad E^0_{Cu^{2+}/Cu} = +\,o.34\ V$

Thus, standard electrode potential of copper electrode is + o.34 V.

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Nernst Equation for Single Electrode Potential

Nernst equation gives the effect of temperature and concentration on electrode potential of an electrode. Let, an electrode involves following electrode reaction of reduction-

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

Following Nernst equation, the electrode potential of this electrode in a condition other than standard condition will be as follows-

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[PRODUCTS]}{[REACTANTS]}$$

$$\therefore \quad E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

Where, $E^0_{M^{n+}/M}$ = standard electrode potential of the electrode

$E_{M^{n+}/M}$ = electrode potential of the electrode in a condition other than Standard condition

n = Number of electrons involved in electrode reaction

R = Gas constant ($8.314 JK^{-1}mol^{-1}$)

F = Faradey's constant (96500 Coulombs)

T = Absolute temperature

By conventions, [M(s)] = 1

$$\therefore \quad E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}(aq)]} \quad \text{-------} \quad (1)$$

$$\text{or} \quad E_{M^{n+}/M} = E^0_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}(aq)] \quad \text{-------} \quad (2)$$

Changing the base of logarithms from e to 10, we get-

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}(aq)]} \quad \text{-------} \quad (3)$$

$$\text{or} \quad E_{M^{n+}/M} = E^0_{M^{n+}/M} + \frac{2.303RT}{nF} \log [M^{n+}(aq)] \quad \text{-------} \quad (4)$$

At 298K temperature, we get following simplified form of Nernst equation-

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}(aq)]} \quad \text{-------} \quad (5)$$

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$$\text{or} \quad E_{M^{n+}/M} = E^0_{M^{n+}/M} + \frac{0.059}{n} \log [M^{n+}(aq)] \quad \text{------- (6)}$$

All these equations are Nernst equations for single electrode potential of different electrodes.

Nernst Equation for Cell Potential

Nernst equation gives the effect of temperature and concentration on electrode potential of the electrodes and therefore, it also gives the effect of temperature and concentration on cell potential of the cells. Let us consider following electrochemical cell-

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

The cell reaction occurring in this cell is as under-

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

Following Nernst equation, the cell potential of this electrochemical cell in a condition other than standard condition will be as under-

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[PRODUCTS]}{[REACTANTS]}$$

$$\therefore \quad E_{cell} = E^0_{cell} - \frac{RT}{2F} \ln \frac{[Cu(s)][Zn^{2+}(aq)]}{[Cu^{2+}(aq)][Zn(s)]}$$

Where, E^0_{cell} = standard cell potential of the cell

E_{cell} = cell potential of the cell in a condition other than standard condition

n = Number of electrons involved in electrode reaction

R = Gas constant ($8.314 JK^{-1}mol^{-1}$)

F = Faradey's constant (96500 Coulombs)

T = Absolute temperature

By conventions, $[Zn(s)] = [Cu(s)] = 1$

$$\therefore \quad E_{cell} = E^0_{cell} - \frac{RT}{2F} \ln \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]} \quad \text{------- (1)}$$

$$\text{or} \quad E_{cell} = E^0_{cell} + \frac{RT}{2F} \ln \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]} \quad \text{------- (2)}$$

Changing the base of logarithms from e to 10, we get-

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$$E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]} \quad \text{------- (3)}$$

$$\text{or} \quad E_{cell} = E^0_{cell} + \frac{2.303RT}{2F} \log \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]} \quad \text{------- (4)}$$

At 298K temperature, we get following simplified form of Nernst equation-

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]} \quad \text{------- (5)}$$

$$\text{or} \quad E_{cell} = E^0_{cell} + \frac{0.059}{2} \log \frac{[Cu^{2+}(aq)]}{[Zn^{2+}(aq)]} \quad \text{------- (6)}$$

All these equations are Nernst equations for cell potential of zinc-copper cell.

Similarly, for following electrochemical cell-

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

The cell reaction occurring in this cell is as under-

$$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

Following Nernst equation, the cell potential of this electrochemical cell in a condition other than standard condition will be as under-

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[PRODUCTS]}{[REACTANTS]}$$

$$\therefore E_{cell} = E^0_{cell} - \frac{RT}{2F} \ln \frac{[Cu^{2+}(aq)][Ag(s)]^2}{[Cu(s)][Ag^{+}(aq)]^2}$$

By conventions, $[cu(s)] = [Ag(s)] = 1$

$$\therefore \quad E_{cell} = E^0_{cell} - \frac{RT}{2F} \ln \frac{[Cu^{2+}(aq)]}{[Ag^{+}(aq)]^2} \quad \text{------- (1)}$$

Changing the base of logarithms from e to 10, we get-

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{2F} \log \frac{[Cu^{2+}(aq)]}{[Ag^{+}(aq)]^2} \quad \text{------- (2)}$$

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At 298K temperature, we get following simplified form of Nernst equation-

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \frac{[Cu^{2+}(aq)]}{[Ag^{+}(aq)]^2} \quad \text{------- (3)}$$

All these equations are Nernst equations for cell potential of copper-silver cell.

Batteries

These are the source of electrical energy which contains either one cell or a number of cells connected in series.

A good quality battery should be light and compact. Its voltage should not vary appreciably during its use.

(1) Primary Batteries

In these batteries cell reactions occur only once. Hence, after use over a period of time they become dead and therefore, they cannot be reused again. For example, Dry cell (Leclanche cell), mercury cell etc.

(1) Dry cell (Leclanche cell)-

Anode- Zinc container

Cathode- Graphite rod surrounded by MnO_2 powder

Electrolyte- Paste of NH_4Cl and $ZnCl_2$

Anode reaction-

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

Cathode reaction-

$$2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$$

Net reaction-

$$Zn(s) + 2NH_4^+(aq) \rightarrow Zn^{2+}(aq) + 2NH_3(g) + H_2(g)$$

Here, hydrogen produced at cathode is oxidized by MnO_2 into MnO(OH), while ammonia produced combines with zinc ions to form complex ion.

$$2MnO_2(s) + H_2(g) \rightarrow 2\,MnO(OH)$$

$$Zn^{2+}(aq) + 4NH_3(g) \rightarrow [Zn(NH_3)_4]^{2+}$$

Cell Potential- 1.25 – 1.50 V

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(2) Mercury cell

Anode- Zn-Hg Amalgam

Cathode- Paste of (HgO + C)

Electrolyte- Moist paste of (KOH+ZnO)

Anode reaction-

$$Zn(Hg) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$$

Cathode reaction-

$$HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$$

Net reaction-

$$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$$

Cell Potential- 1.35 V

(2) Secondary Batteries

These cells can be recharged and therefore, they can be used again and again. For example, Lead storage battery, Nickel-cadmium storage cell etc.

(1) Lead storage Battery

Anode- Compressed spongy lead

Cathode- Grid of lead packed with PbO_2

Electrolyte- 38% H_2SO_4 by mass

Anode reaction-

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

Cathode reaction-

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

Net reaction-

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

Here, cell reaction gets reversed during recharging.

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

Cell Potential- 2.041 V

(2) Nickel-cadmium storage cell

Anode- Cadmium

Cathode- Metal grid containing NiO_2

Electrolyte- KOH solution

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Anode reaction-

$$Cd\ (s) + 2OH^-\ (aq) \rightarrow Cd(OH)_2(s) + 2e^-$$

Cathode reaction-

$$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s)$$

Net reaction-

$$Cd\ (s) + NiO_2(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Here, cell reaction gets reversed during recharging.

Cell Potential- 1.4 V

Fuel Cells

"Such cells which convert energy of combustion of fuel like H_2, CH_4, CH_3OH etc. directly into electrical energy are called fuel cells.

Fuel cells are pollution free and have high efficiency.

Hydrogen-Oxygen Fuel Cell

Electrodes- Porous graphite impregnated with catalyst like Pt, Ag or a metal oxide.

Electrolyte- Aqueous solution of KOH or NaOH

Hydrogen and oxygen are continuously fed into the cell.

At anode-

$$2H_2\ (g) + 4OH^-\ (aq) \rightarrow 4H_2O(l) + 4e^-$$ (**Oxidation)**

At cathode-

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$ (**Reduction)**

Net reaction-

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Cell Potential- 1.0 V

Thermodynamic Efficiency of Fuel Cell

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

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Corrosion of Metals

Slow oxidation of metals to form their oxides and hydroxides, carbonates, sulphides etc. by reaction with moisture and other atmospheric gases is called corrosion.

For example, rusting of iron, blackening of silver, formation of green coatings over copper articles etc. In fact, corrosion is the deterioration of metals by electro-chemical processes where, oxidation of metals occurs in presence of a suitable electron acceptor, called depolarizer. Depolarizers remove electrons from metals. The most common depolarizers are oxygen, acids and less reactive metal ions.

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

$$2H^+ + 2e^- \rightarrow 2H_2O$$

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

Almost all the metals undergo corrosion. Corrosion requires following 3 factors -
(1) Air or oxygen
(2) Moisture
(3) Acidic medium

If anyone of these three factors is missing, corrosion does not occur.

Mechanism of Rusting

Corrosion of iron is called rusting of iron.

$$2Fe\ (s) + \frac{3}{2} O_2\ (g) + xH_2O(l) \rightarrow \underset{\text{(Rust)}}{Fe_2O_3.xH_2O\ (s)}$$

Rusting occurs due to formation of corrosion couples in metals. Here, pure region of the metal act like anode while, the impure region acts like cathode. First, the metal atoms of anode lose their valence electrons and get oxidized to metal ions. These metal ions dissolve in the moisture film in presence of oxygen to form hydrated iron oxides called rust while, the electrons migrate to cathode where they are taken up by a depolarizer.

Oxygen is the most common depolarizer and forms hydroxide ions which finally combine with the Fe^{2+} to form hydrated iron oxides called rust.

The moisture containing dissolved CO_2 acts as electrolyte for corrosion. Here, CO_2 combines with water to form carbonic acid which ionizes further to give H^+ ions.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

The electrode reactions and overall reaction involved in Corrosion of iron (rusting of iron) are as under-

At anode-

$$2Fe\ (s) \rightarrow 2\ Fe^{2+}(aq) + 4e^{-} \quad \text{(oxidation)}$$

At cathode-

$$O_2(g) + 4H^{+}\ (aq) + 4e^{-} \rightarrow 2H_2O(l) \quad \text{(reduction)}$$

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

(overall reaction)

At surface-

$$2\ Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \rightarrow 2Fe_2O_3(s) + 8H^{+}\ (aq)$$

$$Fe_2O_3(s) + xH_2O \rightarrow Fe_2O_3.xH_2O$$

(Rust)

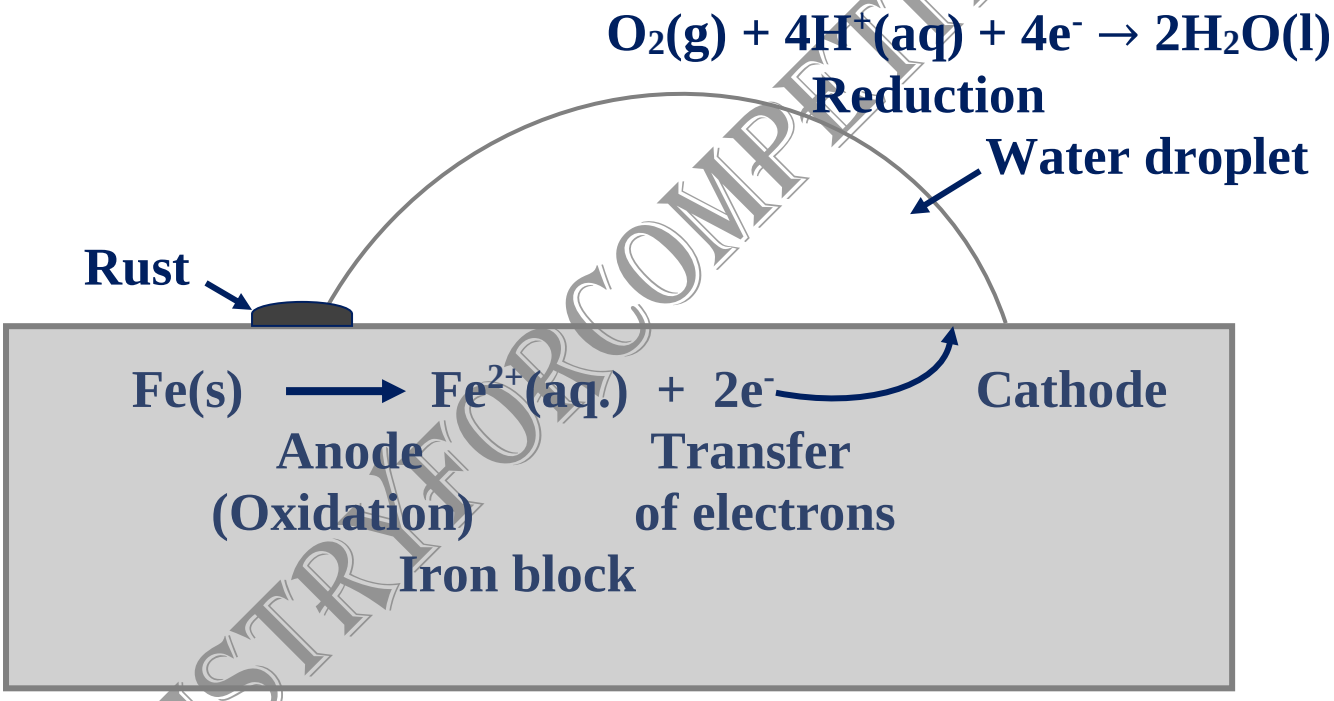


Fig.- Schematic representation of Rusting

Factors affecting Corrosion-

(1) Reactivity of Metal
(2) Presence of moisture and other atmospheric gases like CO_2, SO_2 etc.
(3) Presence of impurities
(4) Presence of electrolytes
(5) Stress in metal

Prevention or control of corrosion

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Both anodic and cathodic processes are required to take place for corrosion to occur. Hence, corrosion can be prevented by preventing either one or both the processes. The most common method is to stop both the processes by painting or applying other protective coating over the object. A more sophisticated method is to keep a slight negative charge over the metal (cathodic condition) and therefore, making following anodic reaction more difficult to take place.

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

Some most common methods applied for prevention of corrosion are as under-

(a) By painting- If the article is painted with a suitable paint, it becomes protected from the contact of air and moisture and therefore, gets protected from corrosion.

(b) Protection using alkaline solution- Here, the article is kept in an alkaline solution so that it gets protected from corrosion.

(c) Electrochemical protection- Here, either anodic or cathodic or both the processes are checked. It may be of following types-

(i) Sacrificial protection- In this method, the article to be protected is coated with a more reactive metal. Here, upper coating corrodes but metal inside gets protected from corrosion.

The coating of zinc over a metal surface is called galvanization. It is the most common method of protecting steel from corrosion. Here, zinc coating being more reactive than iron, corrodes preferentially and protects iron from corrosion. Dissolution of this sacrificial coating of zinc leaves behind electrons which concentrate in the iron, making it cathodic and therefore, inhibits its dissolution.

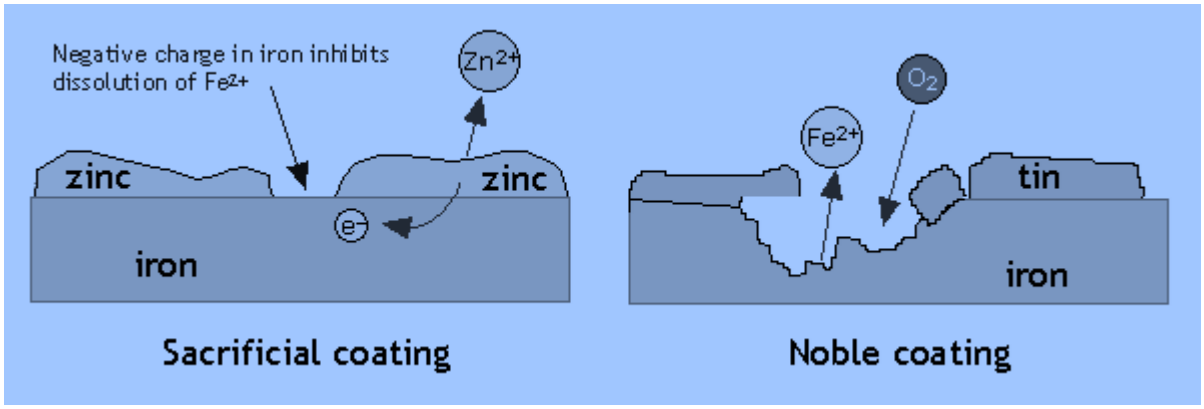


Fig.-Sacrificial and Noble Coating over iron

On the other hand, if the iron is coated with a less reactive metal such as tin (Noble coating) then, as long as the tin coating remains intact no corrosion occurs, but exposure of even a tiny part of the underlying iron to the moist

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atmosphere initiates corrosion. The electrons released from the iron flow into the tin and makes the iron more anodic. Thus, tin actively promotes corrosion of the iron when coating is broken.

(ii) Cathodic protection- In this method, the object is kept in cathodic condition i.e. a negative electrical charge is maintained on the metal, so that its dissolution as positive ions is inhibited. Since in this method, the entire metal surface is kept in the cathodic condition, it is called cathodic protection. This method is especially used in protection of those metallic articles which remain buried in soil.

Here, the source of electrons can either be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or the preferential corrosion of another more active metal such as a piece of zinc or aluminium buried nearby in the ground. Here, metal is connected to an another metal which is more reactive (i.e. more easily oxidisable) so that, this metal oxidizes preferentially and less reactive metal gets protected from corrosion. For example, to avoid corrosion, iron article are connected with a piece of magnesium, where magnesium undergoes corrosion and iron gets protected from corrosion.

Some common observations about corrosion

Corrosion usually starts from a location where the metal is under stress such as bend or weld where two pieces of metal are joined. Which parts of the metal would act as anode depends on many factors and it is revealed by irregular corrosion patterns that are commonly observed. In general, pure region of the metal usually acts like anode while, the impure region acts like cathode. Similarly, the metal atoms in regions that have undergone stress during machining of the formation of articles, usually have higher free energy and therefore, they tend to act like anode.

The oxygen-deprived locations of metals also tend to act like anode and it has been revealed by a number of corrosion patterns. In fact, most of the metals remain covered with a thin oxide film, which inhibits anodic dissolution of these metals. When corrosion occurs, it makes a narrow hole or pit in the metal. The bottom of these pits is deprived of oxygen and therefore, promotes further growth of the pit into the metal.

If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this protected region becomes the most active site for corrosion.

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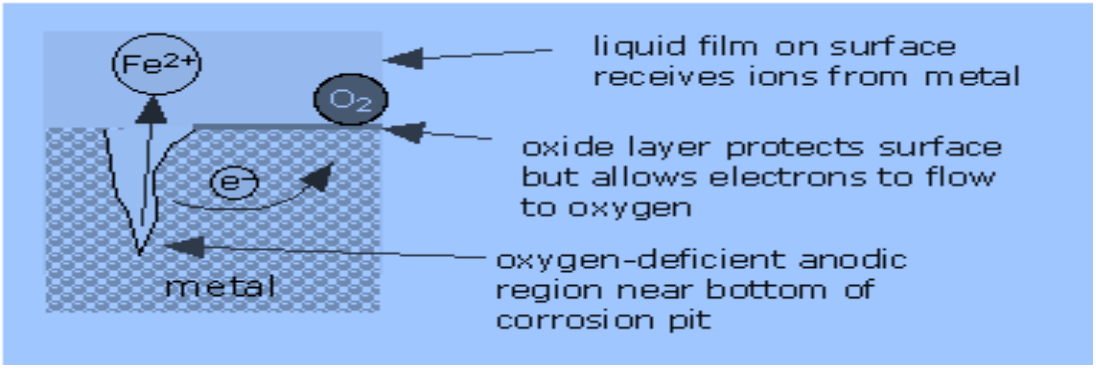


Fig.-Pitting corrosion

In contrast to anodic sites, which tend to be localized to specific regions of the metal surface, the cathodic part of the process can occur almost anywhere. Since, most of the metallic oxides are semiconductors, the oxide coatings do not inhibit the flow of electrons to the surface. Thus, almost all the regions that are exposed to O_2 or to some other electron acceptor can act as a cathode.

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