

Electrochemistry

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Syllabus

- Transport number, determination by Hittorf's method
- Types of electrodes, Electrode/Cell potential, Nernst equation Problems to be solved
- Applications of Nernst equation: electrode/cell potential, equilibrium constant, solubility product and pH, and problems based on them
- Frost & predominance diagram and applications, Modern batteries: Zn-air battery, Li- ion battery
- Cont. Ni-MH battery, Fuel cells (AFCs, PEMFs, SOFCs, MCFCs) (Their construction, working and reactions)
- Corrosion: mechanism of dry and wet corrosion, types of wet corrosion (Galvanic, Concentration, Stress and Pitting).
- Factors affecting and prevention of corrosion

Arrhenius Theory of Ionisation

Arrhenius theory the **conductivity** of solution states that the conductivity in a solution arises due to the presence of ions and may be stated as:

1. When dissolved in water, neutral **electrolytes** are split up into two types of charged particles, **cations and anions**.
2. The ions present in solution **constantly reunite** to form neutral molecules.
3. The charged ions are **free to move** through the solution to the oppositely charged electrode.
4. The electrical conductivity of an electrolyte solution depends on the **number of ions** present in solution.

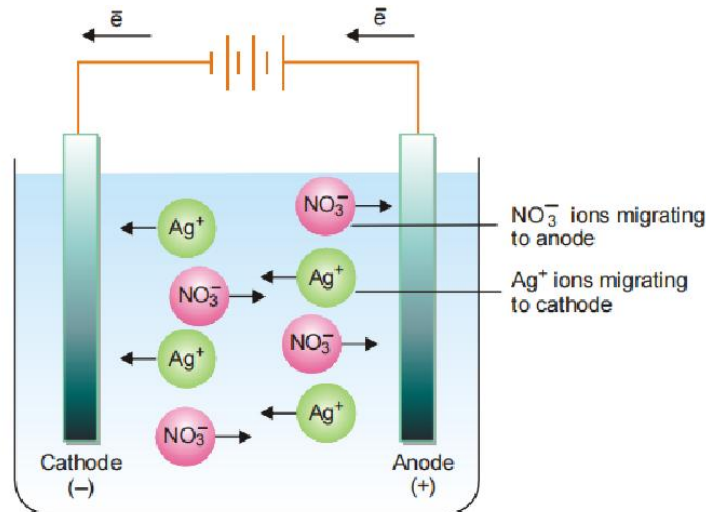
Migration of ions in a solution

Electrolytes splits into cations and anions:



Positive ions tends to migrate/move towards cathode (negatively charged electrode), and anions migrate towards Anode (positively charged electrode)

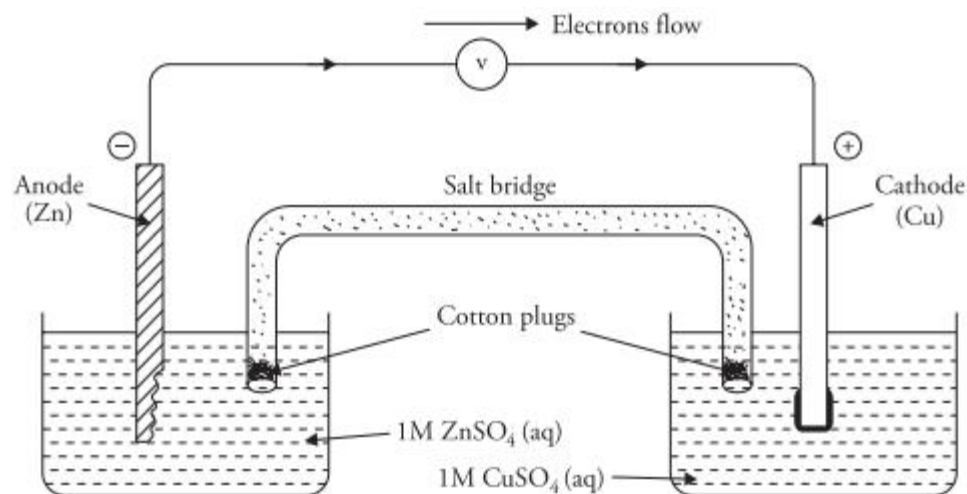
Note that their rate of movement or velocity will be different and depends of the nature of the cation or anion, and the voltage



Electrochemical Cell

- An electrochemical cell is a device which converts chemical energy into electrical energy and vice versa.
- It consists of two electrodes immersed in one or more suitable electrolytes. When these electrodes are connected externally, oxidation and reduction reactions occur.
- The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is called the cathode.
- There are two half half cells, anodic and cathodic half cells.
- An electrochemical cell that produces electricity as a result of chemical reactions is termed as the **galvanic cell**. In a galvanic cell a spontaneous reaction occurring inside the cell produces electricity
- An electrochemical cell in which electrical energy brings about chemical reaction is termed as the **electrolytic cell**. The reactions inside an electrolytic cell are non-spontaneous driven by an external source of current.

Galvanic cell (Daniel Cell)



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

At cathode $\text{Cu}^{2+}(\text{aq}) + 2e^{-} \rightarrow \text{Cu(s)}$ (Reduction)

Oxidation occurs at the anode (– ve terminal)

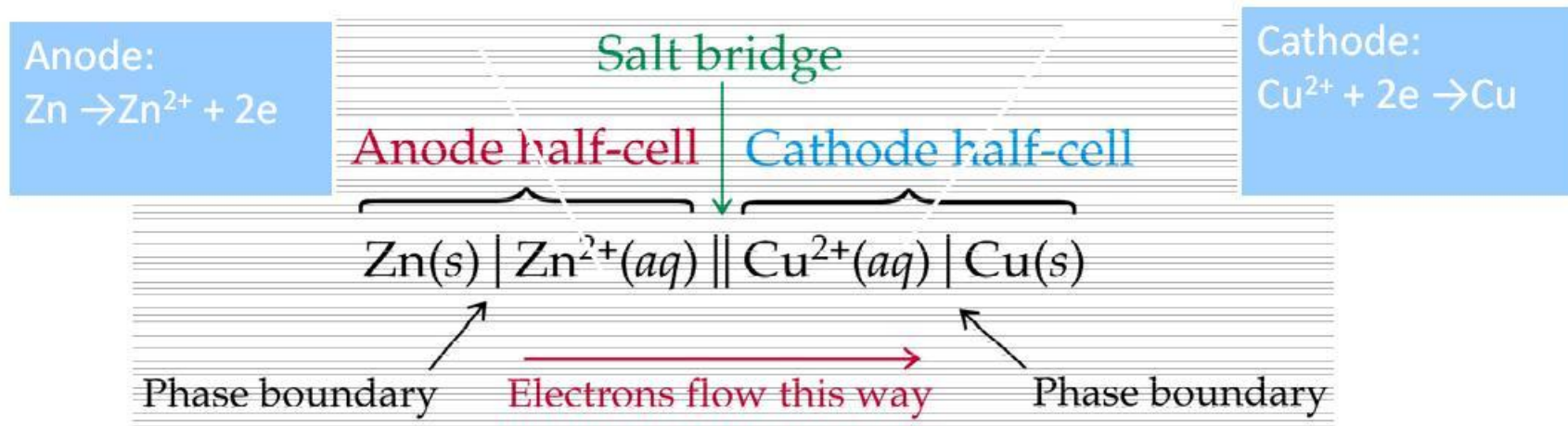
Reduction occurs at the cathode (+ ve terminal)

Electrons flow from the anode to the cathode

Current produced or current consumed

- In **Galvanic (or voltaic) cell** are based on spontaneous process and it generates current (potential capable of performing work)
- In **electrolytic cell** chemical reactions occurs by application of an external potential – **energy consumed**

How to write an electrochemical cell reaction



- (1) The anode is always written on the left and the cathode is always written on the right-hand side.
- (2) The anode of the cell is represented by writing the metal or solid phase first and then the electrolyte (or cation of the electrolyte) while the cathode is represented by writing the electrolyte first (or cation) and then, the metal or solid phase.
- (3) The metal and the cation are separated either by a vertical line (/) or by a semicolon (;)
- (4) The salt bridge which separates the two half cells is indicated by a double line (//).

Electrode Potential and EMF of a Galvanic Cell

When a metal strip (electrode) is dipped in a solution of its own salt, for example a Zn rod is dipped in a solution of ZnSO_4 or a Cu rod is dipped in a solution of CuSO_4 then the following processes may occur (here reactions for Zn strip in a solution of ZnSO_4 are described and similar reactions will occur for Cu strip in contact with CuSO_4 solution).

- The Zn strip loses electrons



The Zn^{2+} ions will go into the solution and the electrons will remain on the Zn strip. In such a case, the zinc strip acquires a negative charge with respect to the solution.

- The Zn^{2+} ions in solution acquire electrons from the Zn strip.



If the metal has a greater tendency to lose electrons and get oxidized it is termed as the *oxidation potential* (like in case of Zn metal in contact with ZnSO_4 solution) and if its ions have a greater tendency to accept electrons and get reduced then it is termed as the *reduction potential* (like in case of Cu metal in contact with CuSO_4 solution).

Electrode Potential and EMF of a Galvanic Cell

Therefore, the EMF or cell potential arises from the difference in the tendency of the two ions to get reduced. It is expressed as

EMF = Reduction potential of cathode – Reduction potential of anode

$$\text{or, } E_{\text{cell}} = E_{(\text{cathode})} - E_{(\text{anode})}$$

∴ Cathode is always written on the right-hand side and anode on the left-hand side, EMF of a cell may also be written as

$$E_{\text{cell}} = E_{(\text{right})} - E_{(\text{left})}$$

It is important to note that a cell reaction will be feasible only if the value of the E_{cell} is positive. A positive value of E_{cell} means that the reaction is thermodynamically favourable and ΔG will be negative making the reaction spontaneous. If the value comes out to be negative, the cell reaction is not possible and the electrodes will have to be reversed in order to bring about the cell reaction.

The cell potential or EMF of a cell can be measured with the help of a potentiometer.

Note: Cell potential was earlier called electromotive force. This term is still widely used; however, IUPAC recommends the term cell potential over electromotive force (emf).

Salt bridge

The *salt bridge* completes the electrical circuit and allows *ions* to flow through both half-cells.

The salt bridge maintains electrical neutrality by allowing excess Zn^{2+} ions to enter from the anode, and excess negative ions to enter from the cathode.

A salt bridge contains nonreacting cations and anions, often K^+ and NO_3^- , dissolved in a gel.

Agar—agar mixed with (KCl , KNO_3 , NH_4NO_3) etc.

Cell Potentials

$$\begin{aligned}E_{\text{cell}} &= E_{\text{red}} (\text{cathode}) - E_{\text{red}} (\text{anode}) \\&= +0.34 \text{ V} - (-0.76 \text{ V}) \\&= +1.10 \text{ V}\end{aligned}$$

Single electrode potential:

The potential of a single electrode in a half-cell is called the single electrode potential.

Standard EMF of a cell (E°)

The emf of a cell with 1 M solutions of anodic and cathodic solution measured at 25 °C and 1 atm pressure.

Measurement of Electrode Potential

It is impossible to determine the electrode potential of a single electrode (i.e., an electrode in contact with its own salt solution).

-
- The electrode potential of an electrode can be determined by combining it with other electrode called the reference electrode to form a complete cell.
- *A reference electrode* is an electrode of standard potential with which we can compare the potentials of other electrodes. Its potential is constant and does not depend on the analyte.
- Standard hydrogen electrode (SHE) is the most commonly used reference electrode.
- The other reference electrodes are calomel electrode, silver–silver chloride electrode, etc.

Selected Standard Electrode Potentials (298 K)

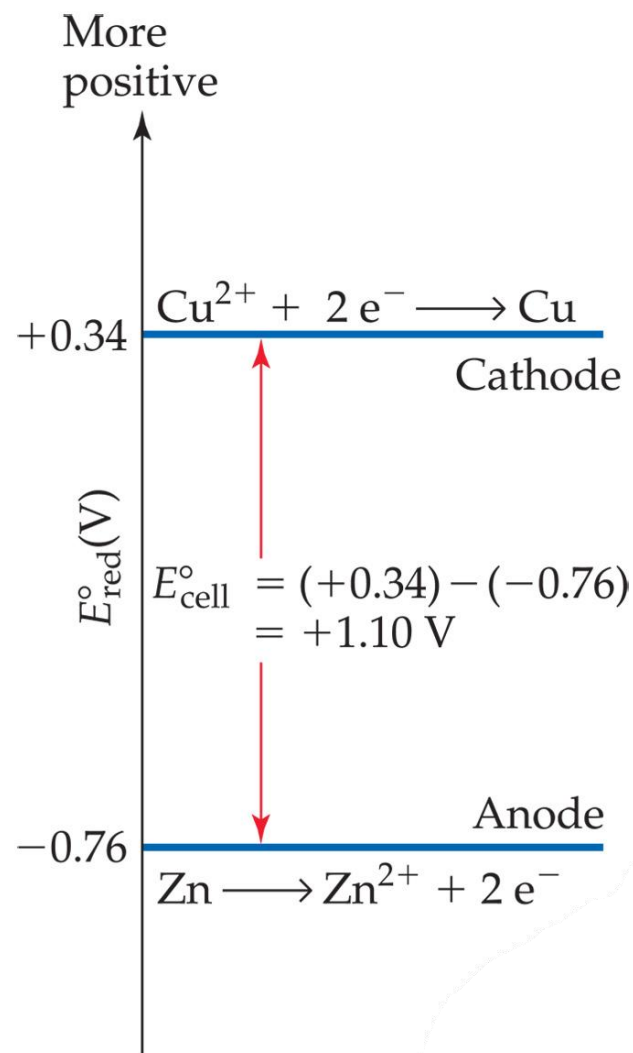
| Half-Reaction | $E^\circ(\text{V})$ |
|----------------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| $\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$ | +2.87 |
| $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$ | +1.36 |
| $\text{MnO}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ | +1.23 |
| $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ | +0.96 |
| $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$ | +0.80 |
| $\text{Fe}^{3+}(\text{g}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ | +0.77 |
| $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$ | +0.40 |
| $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ | +0.34 |
| $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ | 0.00 |
| $\text{N}_2(\text{g}) + 5\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons \text{N}_2\text{H}_5^+(\text{aq})$ | -0.23 |
| $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$ | -0.44 |
| $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ | -0.83 |
| $\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$ | -2.71 |
| $\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$ | -3.05 |

strength of oxidizing agent

strength of reducing agent

Oxidizing and Reducing Agents

The greater the difference between the two, the greater the voltage of the cell.



Q. Calculate the emf of the cell



Given are :- E^0 values of Ni^{2+}/Ni is -0.25 V , Au^{3+}/Au is 1.5 V ,

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$= 1.5 - (-0.25) = 1.75 \text{ V}$$

Q. The standard oxidation potential E° for the half reaction are given below.



Calculate E° for the following cell reaction $\text{Zn} + \text{Fe}^{++} \rightarrow \text{Zn}^{++} + \text{Fe}$

Solution

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= -0.41 - (-0.76)$$

$$= +0.35 \text{ V}$$

Spontaneity of Electrochemical reactions

Relationship Between Cell Potentials E and Free-Energy Changes ΔG

| Reaction Type | E | ΔG | Cell Type |
|----------------|-----|------------|--------------|
| Spontaneous | + | − | Galvanic |
| Nonspontaneous | − | + | Electrolytic |
| Equilibrium | 0 | 0 | Dead battery |

Q. Given are :- E^0 values of Mg^{+2}/Mg is -2.37V , Zn^{+2}/Zn is -0.76V , Fe^{+2}/Fe is -0.44V . Using this information predict whether Zn will reduce iron or not?

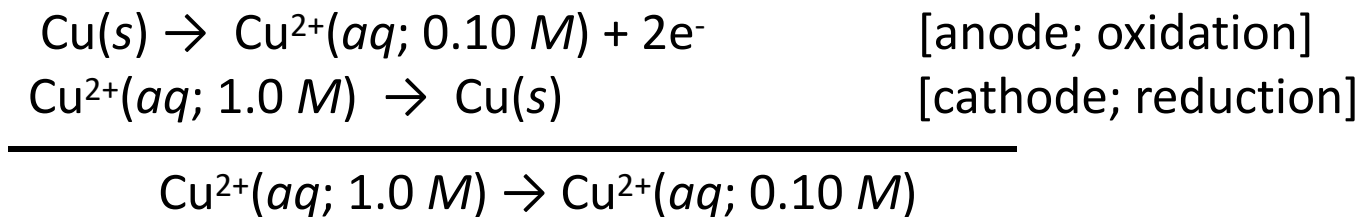
Ans.

**Zinc has lower reduction potential than iron.
hence, it can reduce iron.**

Concentration Cells

A *concentration cell* exploits the effect of concentration changes on cell potential.

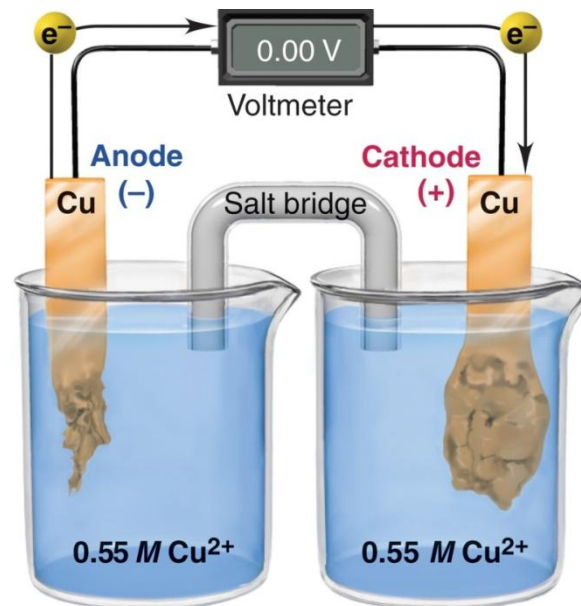
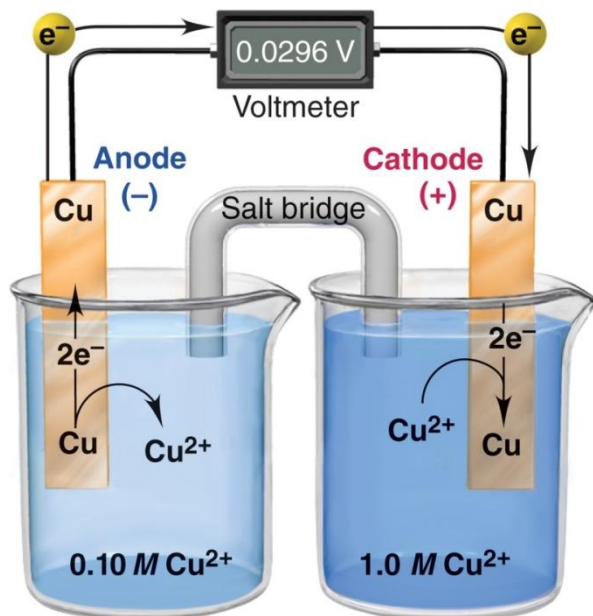
The cell has the same half-reaction in both cell compartments, but with different concentrations of electrolyte:



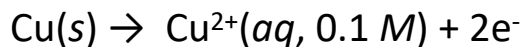
As long as the concentrations of the solutions are different, the cell potential is > 0 and the cell can do work.

A concentration cell based on the Cu/Cu^{2+} half-reaction.

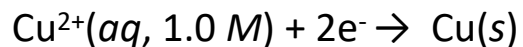
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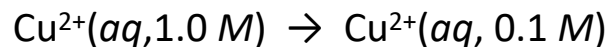
Oxidation half-reaction



Reduction half-reaction



Overall (cell) reaction



$E_{\text{cell}} > 0$ as long as the half-cell concentrations are different.
The cell is no longer able to do work once the concentrations are equal.

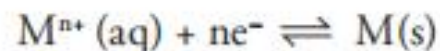
Nernst Equation

The electrode potential of an electrode depends upon the concentration of the electrolyte solution and the temperature. The electrode potential is termed as the standard electrode potential when

- Concentration of electrolyte is 1 M
- Temperature = 298 K
- Pressure of gaseous component is 1 atm or 1 bar (1.00×10^5 Pa)
- Solid components are in their standard states

Nernst equation gives the relationship between the electrode potential and the concentration of the electrolyte solutions.

Consider a general electrode reaction.



For a reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are related by the Van't Hoff reaction isotherm as

$$\begin{aligned}\Delta G &= RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}\end{aligned}\tag{1}$$

ΔG^0 is the standard free energy change (i.e., the change in free energy when the concentration of the reactants and products are unity), R is the gas constant and T is the temperature.

The electrical energy is produced at the expense of the decrease in free energy, that is,

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^0 = -nFE^0$$

where n is the number of electrons liberated at one electrode, F = Faraday's constant ($1F = 96500$ coulomb)

E is the electrode potential and E^0 is the standard electrode potential.

Substituting these values in Equation (1), we have

$$-nFE = -nFE^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{or}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{Product}]}{[\text{Reactant}]} \quad (2)$$

Since electrode reaction is always represented by reduction reaction; hence, we can write Nernst equation as

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

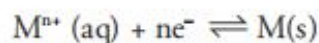
Equation (2) is called the Nernst equation and gives the dependence of electrode potential on the concentration of the electrolyte.

At $T = 298 \text{ K}$, $F = 96500$, $R = 8.314 \text{ J K}^{-1}$, Eq. (2) reduces to

$$E = E^0 - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^0 - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

For the electrode reaction



The equation becomes

$$E = E^0 - \frac{0.0591}{n} \log \frac{[\text{M}(\text{s})]}{[\text{M}^{n+}(\text{aq})]}$$

For pure solids, $[\text{M}(\text{s})] = 1$, and the equation becomes

$$\begin{aligned} E &= E^0 - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}(\text{aq})]} \\ &= E^0 + \frac{0.0591}{n} \log [\text{M}^{n+}(\text{aq})] \end{aligned}$$

For a cell reaction,



The Nernst equation can be written as

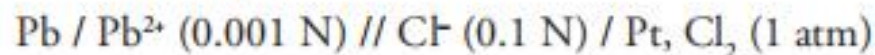
$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

It is evident from the Nernst equation that the electrode potential decreases with rise in temperature.

Applications of Nernst equation

1. **Calculation of cell potential of the cell** Nernst equation is used to calculate the cell potential at given electrolyte concentration

Q1. Calculate the potential for each half cell and the total EMF at 25 °C for the cell represented schematically as



$$E_{\text{Pb}^{2+}/\text{Pb}}^0 = -0.126 \text{ V}; \quad E_{\text{Cl}_2/2\text{Cl}^-}^0 = +1.358 \text{ V}$$

Q2. Write the Nernst equation and calculate the EMF of the following cell at 298 K.



$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V}; \quad E_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.37 \text{ V}$$

2. Calculation of equilibrium constant

Nernst equation can be used to find the equilibrium constant of a given cell.

Consider the equilibrium reaction given below.



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_c is the equilibrium constant.

The Nernst equation can be written as

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K_c$$

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

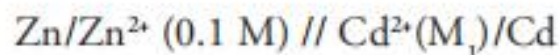
$$0 = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K_c$$

$$\text{or } \log K_c = \frac{nE_{\text{cell}}^0}{0.0591} \text{ at } T = 298 \text{ K}$$

Q3. Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc.
The standard electrode potential of the cell is 1.56 V.

3. **To find the concentration of one ionic species in a cell if the concentration of the other species is known**

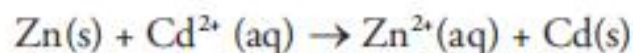
Q4. Find the concentration of Cd^{2+} ions in the given electrochemical cell:



Given: $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$; $E_{\text{Cd}^{2+}/\text{Cd}}^0 = -0.40 \text{ V}$; $E_{\text{cell}} = 0.3305 \text{ V}$ at 298 K

Solution

The cell reaction for the above cell is



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+} (\text{aq})]}{[\text{Cd}^{2+} (\text{aq})]}$$

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$= -0.40 - (-0.76) = 0.36 \text{ V}$$

Substituting this value in the Nernst equation,

$$0.3305 = 0.36 - \frac{0.0591}{2} \log \frac{0.1}{M_1}$$

$$-0.0295 = -0.0295 \log \frac{0.1}{M_1}$$

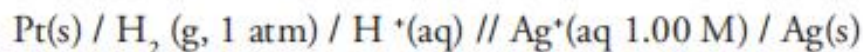
$$\log \frac{0.1}{M_1} = 1 \quad ; \quad \frac{0.1}{M_1} = 1 \text{ antilog}$$

$$\frac{0.1}{M_1} = 10 \quad \text{or} \quad M_1 = 0.01$$

4. **To find the pH of a solution**

Nernst equation can be used to find the pH of a solution

Q5 An electrochemical cell is represented as follows



Given $E = 0.900 \text{ V}$ at 25°C ; $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$

Find the pH of the solution.

Solution

The reactions involved are



According to Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \log \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2}$$

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

$$= 0.80 - (-0) = 0.80 \text{ V}$$

Substituting this value in the Nernst equation, we have

$$0.90 = 0.80 - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{[1 \text{ M}]^2}$$

$$-0.0295 \log [\text{H}^+]^2 = 0.90 - 0.80$$

$$-\log [\text{H}^+]^2 = \frac{0.100}{0.0295} = 3.3898$$

$$-2 \log [\text{H}^+] = 3.3898 \quad \text{or} \quad -\log [\text{H}^+] = 1.6949$$

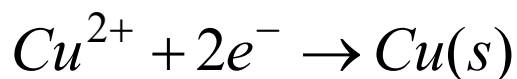
$$\therefore -\log [\text{H}^+] = \text{pH}$$

Hence,

$$\text{pH} = 1.6949$$

Q. Determine the electrode potential when a copper electrode is dipped in a 0.2 M solution of copper sulphate at RT. Given the standard potential of Cu^{2+}/Cu system = 0.34.

Solution:



We know that $E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 + \frac{0.0591}{n} \log_{10} [\text{Cu}^{2+}]$

$$E_{\text{red}} = 0.34 + \frac{0.0591}{2} \log[0.2]$$

$$E_{\text{red}} = 0.34 + 0.02955 \times 0.301$$

$$= 0.39$$

Q. Find the cell potential for the following:

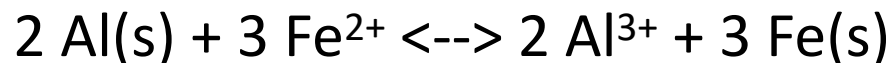
(a) $\text{Al(s)} \mid \text{Al}^{3+} (0.1 \text{ M}) \parallel \text{Fe}^{2+} (0.1 \text{ M}) \mid \text{Fe(s)}$

(b) $\text{Al(s)} \mid \text{A}^{3+} (0.1 \text{ M}) \parallel \text{Fe}^{2+} (0.01 \text{ M}) \mid \text{Fe(s)}$

(c) $\text{Al(s)} \mid \text{A}^{3+} (0.01 \text{ M}) \parallel \text{Fe}^{2+} (0.1 \text{ M}) \mid \text{Fe(s)}$

Given the standard reduction potential of Fe and Al are -1.706 and -0.407 V respectively

Discuss the spontaneity of these reaction



$$n = 6$$

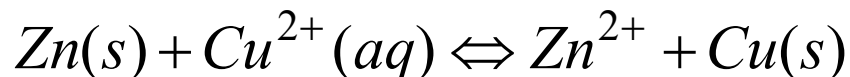
Ans. (a) 1.287 V

(b) 1.257 V (least spontaneous)

(c) 1.30 V (most spontaneous)

Equilibrium constant and cell EMF

Lets consider a electrochemical cell reaction in equilibrium



Applying Nernst equation

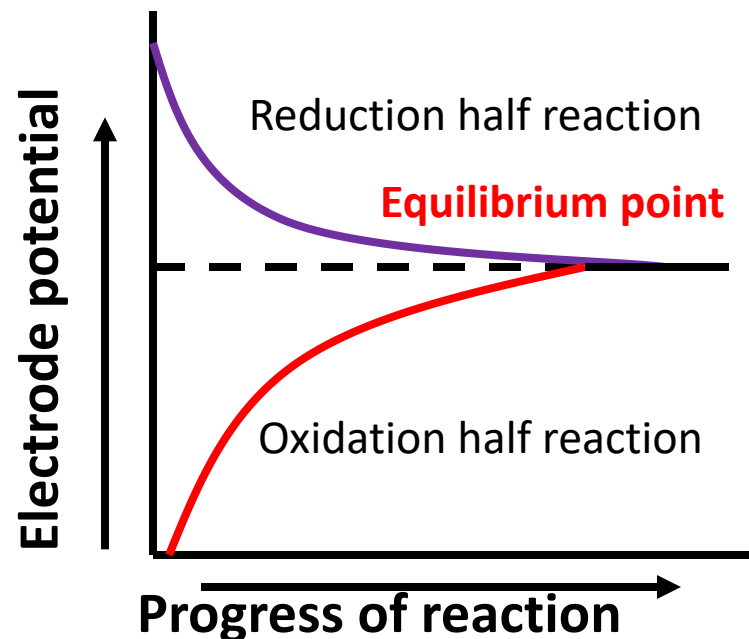
$$E = 0 = E^0(\text{cell}) - \frac{2.303RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E^0(\text{cell}) = \frac{2.303RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

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

Therefore, $E^0(\text{cell}) = \frac{2.303RT}{2F} \log K_c$

Generally, $E^0(\text{cell}) = \frac{2.303RT}{2F} \log K$



$$E_{\text{cell}} = E^o - \frac{0.05916}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Equilibrium constant and cell EMF

- When $K < 1$, [reactant] > [product], $\ln K < 0$, so $E_{cell} > E^\circ_{cell}$
- When $K = 1$, [reactant] = [product], $\ln K = 0$, so $E_{cell} = E^\circ_{cell}$
- When $K > 1$, [reactant] < [product], $\ln K > 0$, so $E_{cell} < E^\circ_{cell}$

Q. Calculate the equilibrium constant of the reaction



$$E^\circ_{cell} = \frac{0.0591}{2} \log[K_c]$$

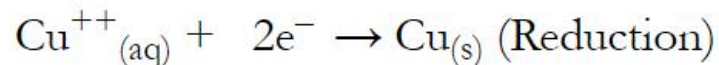
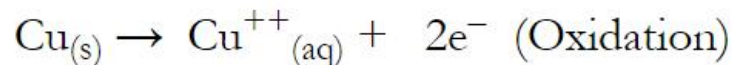
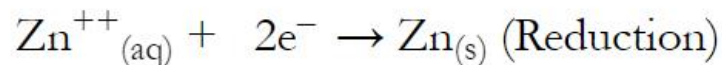
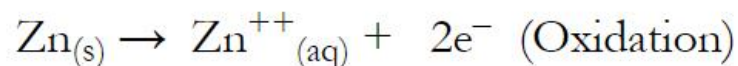
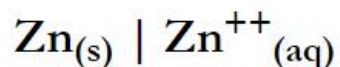
$$\log[K_c] = \frac{0.46 \times 2}{0.0591}$$

$$K_c = 4 \times 10^{15}$$

Types of Electrodes

A wide variety of electrodes are known. They are classified depending upon the nature of the half cell reactions. Some common types of reversible electrodes are discussed below.

1. Metal–metal ion electrode: This type of electrode consists of a metal in contact with a solution of its own ions. These electrodes are also known as electrodes reversible with respect to cations. Common examples are (i) Cu electrode in a solution of CuSO_4 (ii) Zn rod in a solution of ZnSO_4 .



Metal–sparingly soluble metal salt electrode In this type of electrode, the metal is in contact with its sparingly soluble salts and a solution of a soluble salt having an anion common with the sparingly soluble salt. These electrodes are reversible with respect to the anion.

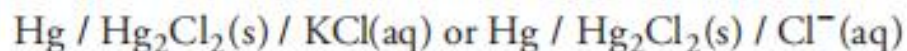
Common examples are

(i) calomel electrode

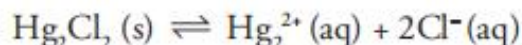
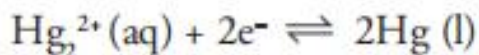
(ii) silver–silver chloride electrode

(iii) lead–lead sulphate electrode.

Calomel electrode: It is commonly used as a secondary reference electrode for potential measurements in place of a hydrogen electrode. The calomel electrode consists of mercury in contact with mercurous chloride Hg_2Cl_2 (calomel) and a solution of soluble chloride ions such as KCl of known concentration.



The half cell reaction is

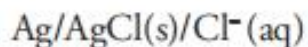


Thus, in case of calomel electrode, the electrode reaction may be represented as

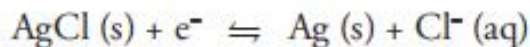


The electrode, therefore is reversible with respect to chloride ion.

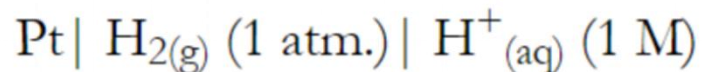
Silver–silver chloride electrode: It consists of a silver wire, coated electrolytically with silver chloride (a highly insoluble salt) and is dipped in a KCl solution.



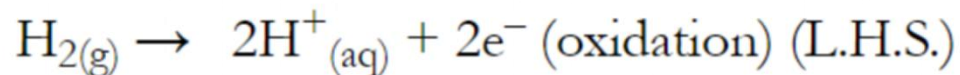
The electrode reaction is

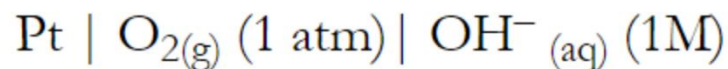


3. Gas electrode: In these electrodes, gases (O_2 or Cl_2) are continuously bubbled through a solution of their corresponding ions, i.e., hydroxyl or chloride ions using an inert metal like Pt or Au to maintain electrical contact. The inert metal is dipped in the solution of hydroxyl or chloride ions and the gas is bubbled. The metal adsorbs the gas and an equilibrium is established between the gas and the ions in the solution. Common examples of this type are the hydrogen electrode, oxygen electrode and chlorine electrode.

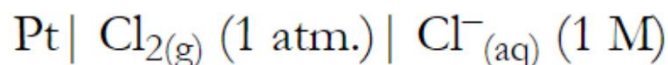
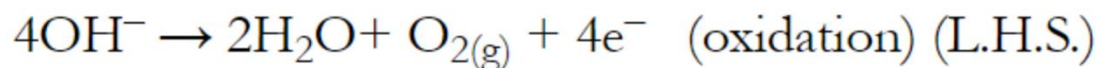


The half cell reactions are

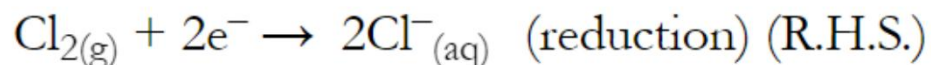
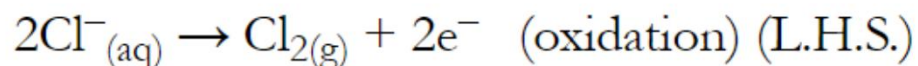




The half cell reaction is



The half cell reactions are



Modern Batteries

A battery is a power source in which several galvanic cells are connected in series or parallel. Like a galvanic cell, a battery also consists of an anode, a cathode and an electrolyte. There are three types of batteries.

Primary batteries: In these batteries, the cell reaction is irreversible, i.e., the reaction taking place in the forward direction cannot be reversed by the application of external potential. Once the cell reaction has taken place and the reactants have been converted into products, the cell gets discharged and cannot be used again.

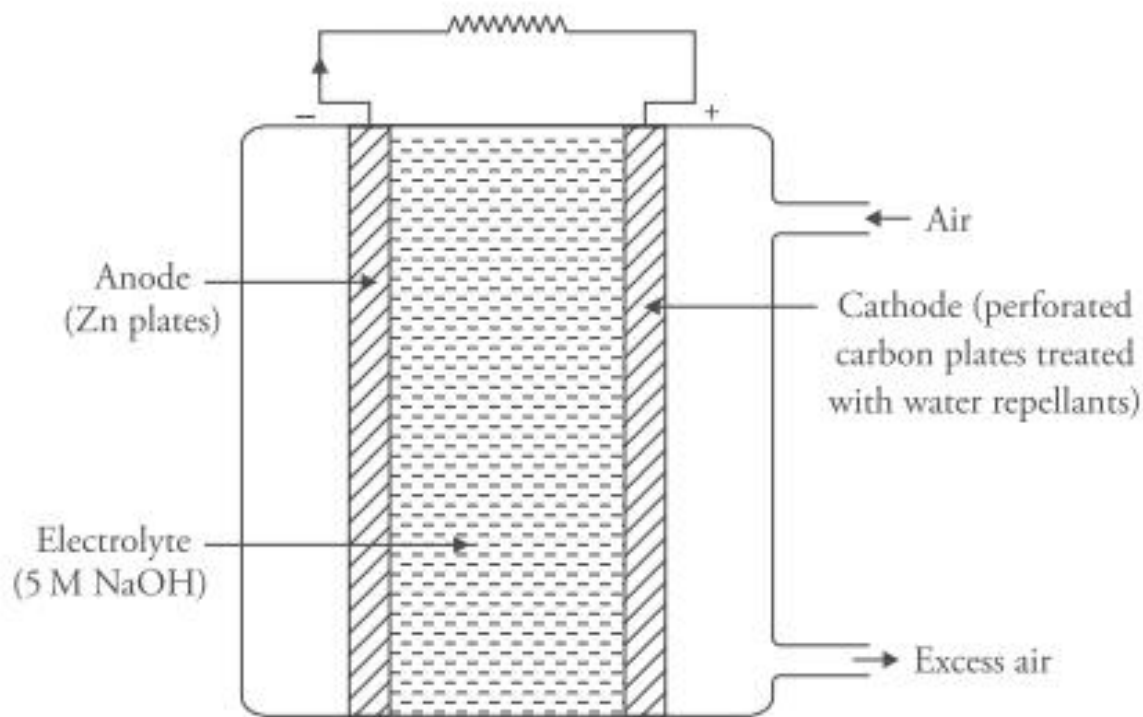
Example: Dry cells or Leclanche cell.

(ii) Secondary batteries: In these batteries, the cell reaction is reversible. Once the forward reaction occurs and the cell is discharged, it can be charged again by applying external potential. They are also called storage cells or rechargeable batteries. Common examples are lead acid batteries used in automobiles, nickel cadmium batteries used in aircraft and railways and lithium ion batteries used in mobile phones

(iii) Reserve batteries: These are batteries which remain in an inactive state and are activated immediately before use. Activation is done by adding the missing component like by the simple addition of water or any other electrolyte. These batteries are very useful in mines, radars, night viewing equipments, artillery, pilot balloons, etc. They should withstand vibration, shock, extreme pressure variation; have a long inactive shelf life and should be rapidly activated when required. Common examples are silver chloride cells which are activated by sea water or even by fresh water.

Zn-Air Battery

In zinc air battery, the anode is made of zinc plates. A perforated carbon plate treated with water repellants acts as a cathode. Sodium hydroxide (5M) or potassium hydroxide is used as an electrolyte. The anode, cathode and the electrolyte are contained in an ebonite or polymeric case. It also has a vent for the entry of air or O_2 into the cell. At the anode, zinc reacts with electrolyte (NaOH or KOH) to form zincate ions which decay into zinc oxide and water. The electrons released at the anode travel to the cathode where oxygen of the air accepts the electrons to form hydroxide ions.



The cell is represented as

Zn / NaOH (5 M) / Air / C

The cell reactions are

At anode $2 \text{Zn (s)} + 4 \text{OH}^- \text{(aq)} \rightarrow 2\text{ZnO(s)} + 2\text{H}_2\text{O (l)} + 4\text{e}^-$

At cathode $\text{O}_2 \text{(g)} + 2\text{H}_2\text{O (l)} + 4\text{e}^- \rightarrow 4\text{OH}^- \text{(aq)}$

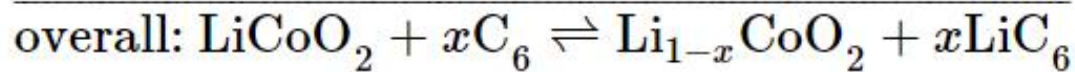
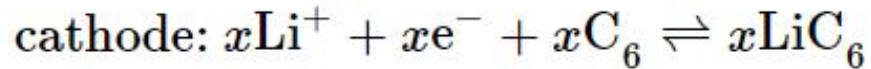
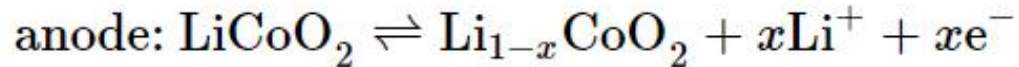
Overall cell reaction $2\text{Zn(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{ZnO (s)}$

Characteristics of Zinc-air batteries

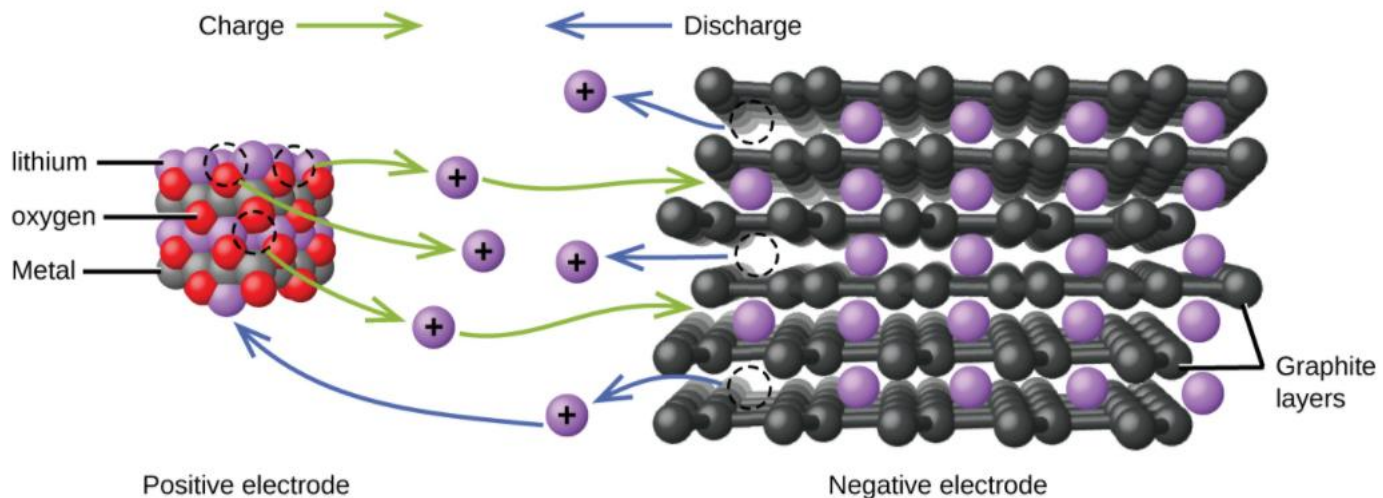
- They produce 1.65 volts.
- Zinc air batteries have the properties of both fuel cell and batteries.
- Zinc air batteries are electrically non-rechargeable, however they can be recharged mechanically by converting the zinc oxide produced in the battery back into zinc metal. This zinc metal can be reused.
- They are very cheap and are increasingly being used instead of mercury batteries.
- Their size varies from small button cells that are used in watches and in hearing aids to large batteries used in cameras and also for the electric propulsion of vehicles.

Li- Ion Battery

Lithium ion batteries are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are



With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.



Advantage of Li⁺ ion Batttery

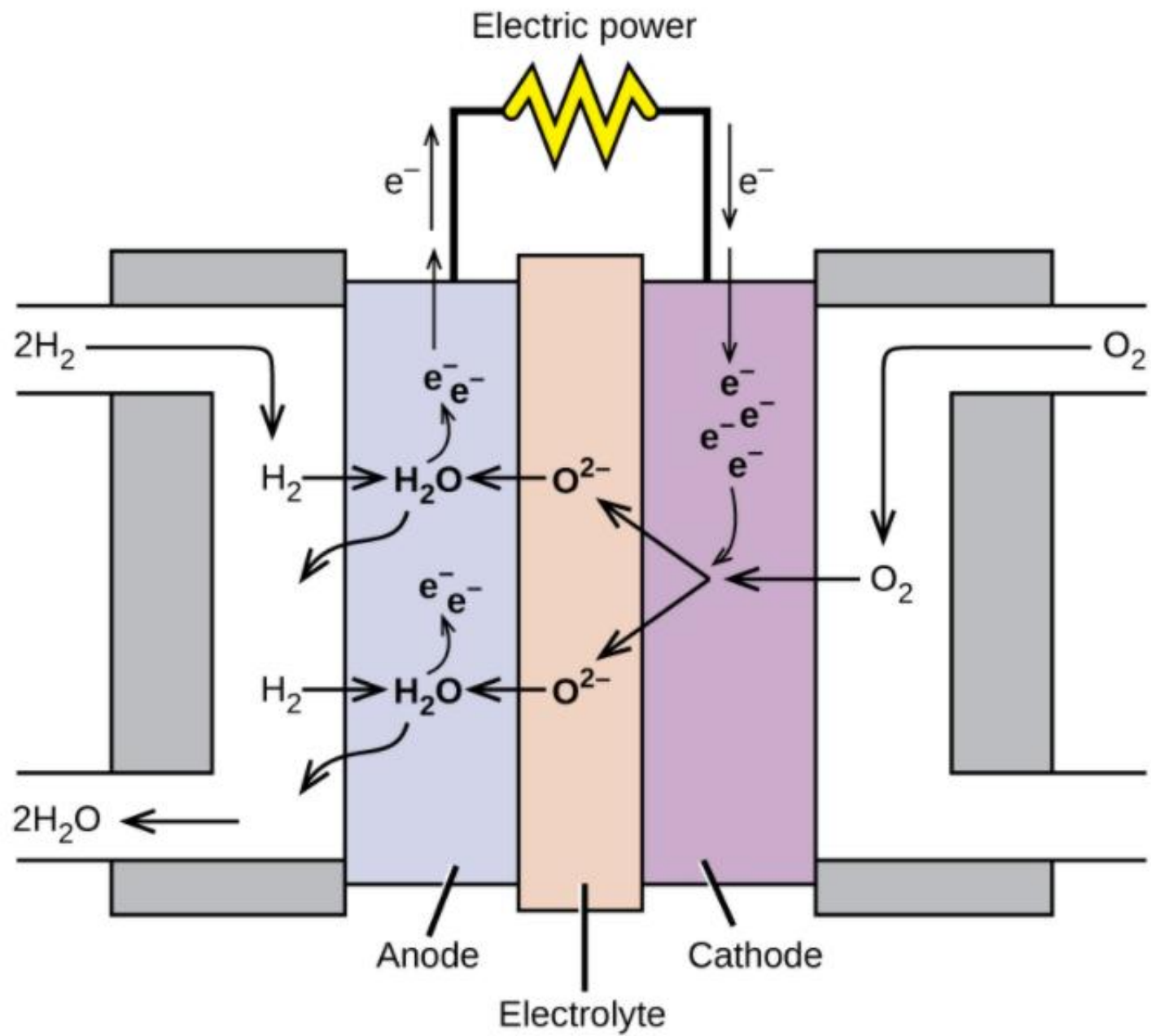
- ❖ Lighter than other rechargeable batteries
- ❖ Higher open-circuit voltage
- ❖ Low self-discharge rate (about 1.5% per month)
- ❖ No battery memory effect
- ❖ Environmental benefits

Disadvantage of Li⁺ ion Batttery

- Poor cycle life in high current applications
- Growing internal resistance with cycling and age
- Safety concerns if overheated or overcharged
- Applications demanding more capacity

Fuel Cells

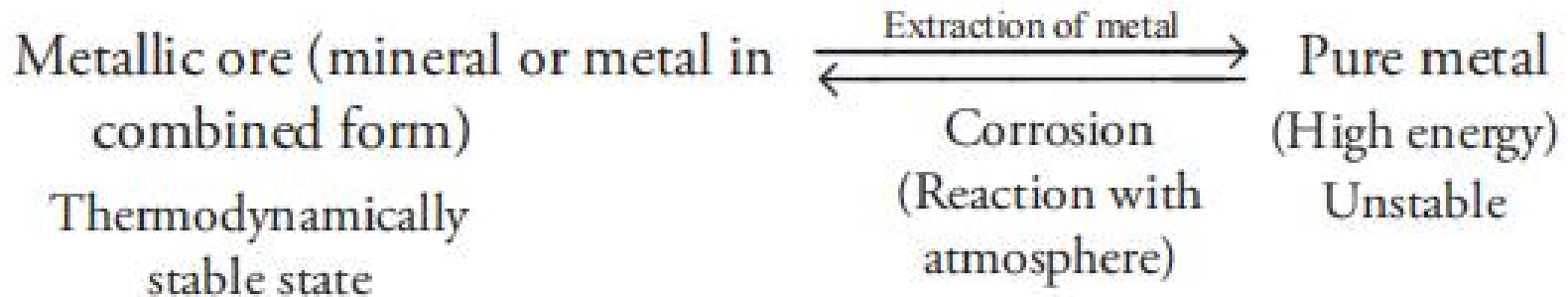
- Fuel cells are energy converters which take chemical substances from the external source and convert them to electrical energy.
- Fuel cell differs from a battery in that the chemical substances are an integral part of a storage battery whereas in fuel cells, they are fed into the cells whenever energy is desired.
- The electrodes used in fuel cells are generally inert but have catalytic properties. The anodic materials used are generally gaseous or liquids (contrary to metal anodes used in batteries).
- In a fuel cell, hydrogen enters at the anode where it loses electrons. These electrons travel to the cathode. Oxygen enters at the cathode. It picks up electrons and either combines with the hydrogen ions that travel from the anode through the electrolyte or travels to the anode through the electrolyte and combines with hydrogen ions.
- The hydrogen and oxygen ions combine to form water which is removed from the cell.
- A fuel cell generates electricity as long as hydrogen and oxygen are supplied to it.
- The electrolyte plays a vital role in a fuel cell. It permits appropriate ions to pass between the anode and cathode.
- Depending on the type of electrolyte used, they can be different types.



Corrosion

The corrosion may be defined as the process of spontaneous deterioration or disintegration of metals (except gold and platinum) caused by direct chemical or indirect electrochemical attack by reaction with the environment.

- e.g., Rusting of iron and formation of a green layer of basic carbonate on the surface of copper.
- Note that the term rusting applies to the corrosion of iron and iron base alloys. Nonferrous alloys corrode but do not rust.

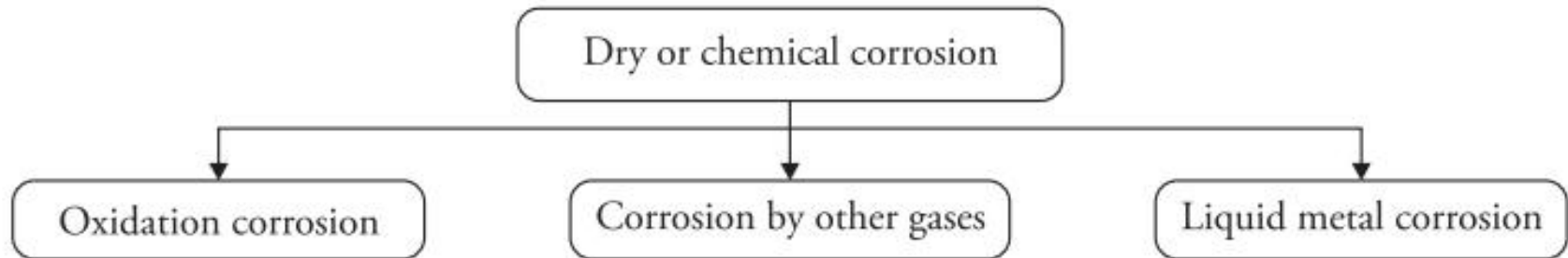


Effects of Corrosion

- (i) Corrosion causes severe economic losses and hampers the safety of equipment. It leads to direct economic losses that occur due to money being spent on maintenance and replacement of the corroded parts. Painting, maintaining cathodic protection devices, cost involved in protection techniques, such as galvanisation, modifying external environment by deaeration and dehumidification, all incur heavy financial losses.
- (ii) Metal loses its useful properties because of corrosion. It can become brittle, leading to the failure of machine parts.
- (iii) Frequent replacement and maintenance of the corroded parts leads to indirect financial losses, which include production loss during replacement and maintenance.
- (iv) Corroded pipes may lead to leakage of inflammable and toxic gases resulting in fire hazards; toxic gases lead to environmental pollution and affect the human and animal population adversely.
- (v) It causes contamination of the products. For examples traces of metals may alter the color of dyes. Food articles in corroded containers may get spoilt due to contamination.
- (vi) It has been estimated that nearly 25% of the annual production of iron is wasted because of corrosion.

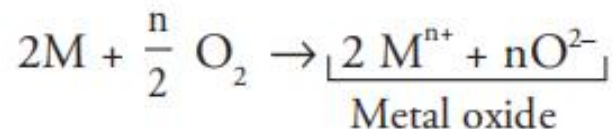
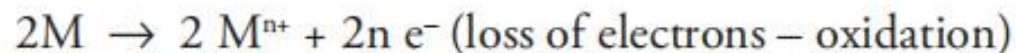
Dry or Chemical Corrosion

Also called direct corrosion, it occurs because of direct chemical action of the environment on the metal surface in the absence of moisture or a liquid electrolyte. It generally occurs at a temperature higher than 100 °C when it is not possible to develop a surface water layer. It is generally of three types:

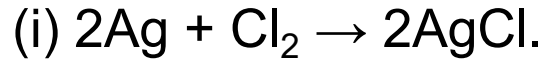


Oxidation Corrosion: It is brought about by the direct action of oxygen on the metal surface at high or low temperature. At low temperature, alkali and alkaline earth metals are oxidized and at high temperatures except Ag, Au and Pt, all other metals are oxidized. It generally takes place in the absence of moisture. For example, copper oxidizes in air at a low temperature of about 260 °C forming a film of Cu₂O. At temperatures between 260 °C and 1025 °C the Cu₂O layer is overlaid by a layer of CuO film. Similarly, iron oxidizes at a low temperature of approximately 250 °C, forming an oxide consisting mainly of Fe₃O₄.

Mechanism: The metal surface reacts directly with oxygen forming an oxide layer. This oxide layer acts as a barrier and prevents further oxidation of the metal. For further oxidation to take place, either the metal must diffuse outward through the oxide layer or oxygen must diffuse inward. Both the transfers occur, but the outward diffusion of the metal ion is faster as the size of the metal ion is smaller than that of the oxygen atom or the O²⁻ ion.



Corrosion by other gases: In this, dry gases like H_2 , Cl_2 , F_2 , SO_2 and CO_2 directly attack the metal surface. Rate of corrosion depends upon the chemical affinity between the metal and gas and also on the nature of the film formed. For example,



The AgCl film is nonporous and protective (volume of the film > volume of the metal) and thus it protects the metal from further attack.



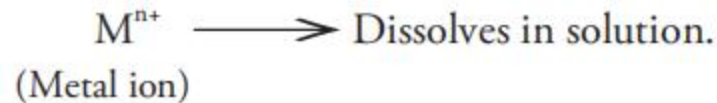
SnCl_4 being volatile, Sn undergoes excessive corrosion. The rest of the mechanism is the same as that of oxidation corrosion.

(iii) H_2S attacks steel forming FeS layer, which is porous in nature.

Liquid metal corrosion It occurs when an anhydrous liquid attacks the metal surface. When a liquid metal flows over a solid metal at high temperature it weakens the solid metal because of

- Its dissolution in liquid metal.
- Penetration of liquid metal into solid metal. For example, sodium metal (coolant) leads to the corrosion of cadmium in a nuclear reactor.

Anodic reactions: Oxidation occurs at the anode; the metal loses electrons and passes them into the solution. Thus, the metal at anode is destroyed by dissolving or by changing into metal ions. *Hence, corrosion always occurs at the anodic areas.*



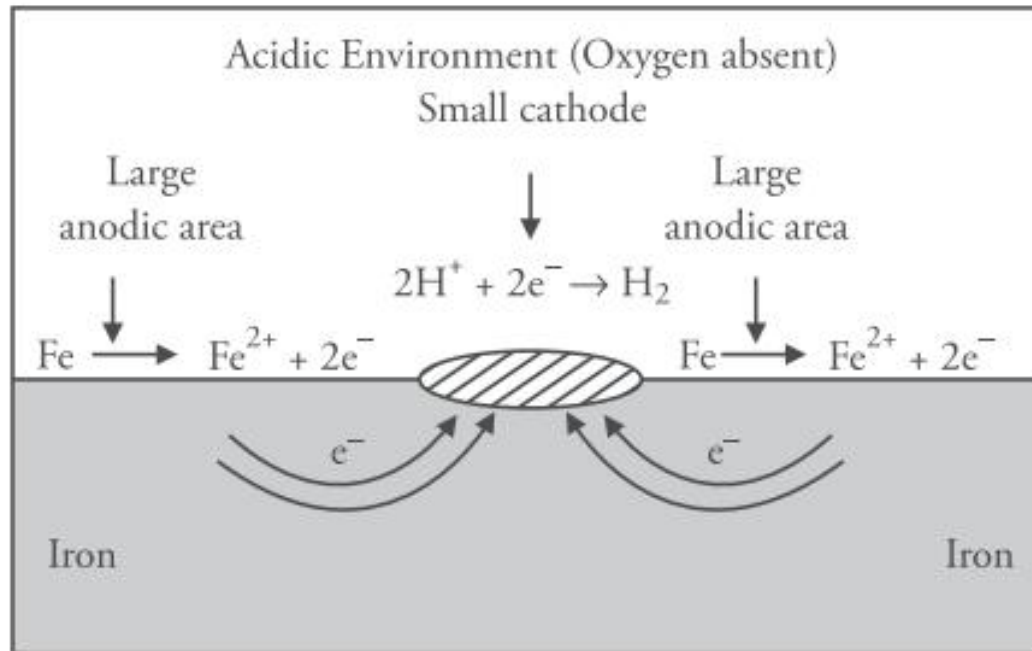
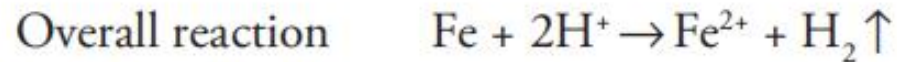
Cathodic reactions: The electrons released at the anodic areas are consumed in the reactions at the cathode. Depending on the nature of the environment, the cathodic reactions are of two types

(i) Evolution of hydrogen: This mechanism usually occurs when anodic areas are large and cathodic areas are small and oxygen is absent.

In acidic medium, the reaction becomes $2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2 \uparrow$

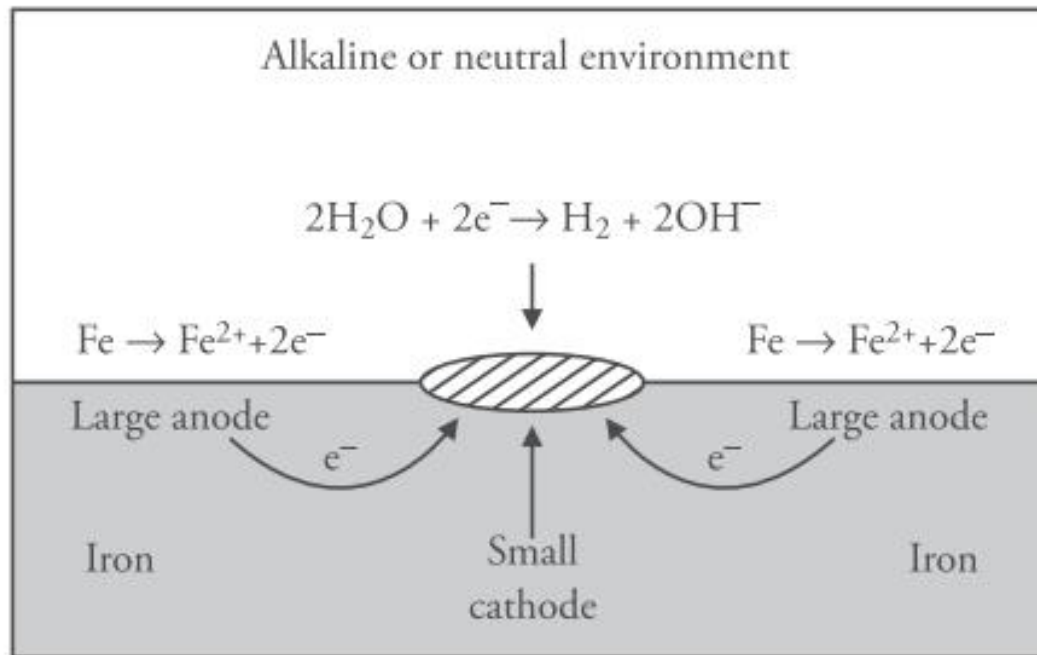
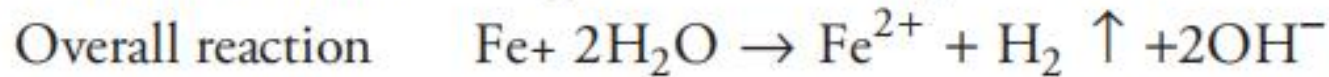
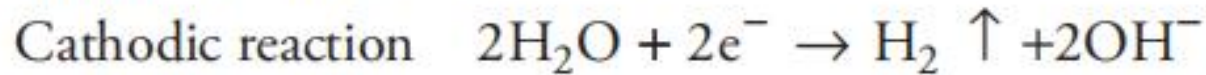
In neutral and alkaline medium, the reaction becomes $2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}$

For example, rusting of iron takes place in acidic medium in the absence of oxygen as follows



The Fe^{2+} ions react with the anion of the acid to form the corrosion product

In neutral or alkaline medium, the following reactions occur



The Fe^{2+} formed at the anode and OH^- formed at the cathode diffuse towards each other and meet to form $\text{Fe}(\text{OH})_2$

Types of wet corrosion (Galvanic, Concentration, Stress and Pitting).

Types of electrochemical corrosion

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graph TD; A[Types of electrochemical corrosion] --> B[Concentration cell corrosion or Differential Aeration Corrosion (DAC)]; A --> C[Differential Metallic Corrosion (DMC) or Bimetallic corrosion]; B --> D[For example, Pitting corrosion, Waterline corrosion, Stress corrosion, Corrosion under a drop of water, leaf, stone, block of wood, etc., Caustic embrittlement, etc.]; C --> E[For example, Galvanic corrosion];
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Concentration cell corrosion
or Differential Aeration Corrosion (DAC)

Differential Metallic Corrosion
(DMC) or Bimetallic corrosion

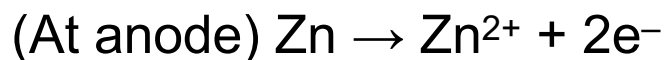
For example,

- Pitting corrosion
- Waterline corrosion
- Stress corrosion
- Corrosion under a drop of water, leaf, stone, block of wood, etc.
- Caustic embrittlement, etc.

For example,
Galvanic corrosion

Galvanic Corrosion It is also called bimetallic corrosion or differential metallic corrosion. It occurs when two dissimilar metals (for example, Zn and Cu) are electrically connected and exposed to an electrolyte and then the metal higher in the electrochemical series undergoes corrosion.

For example, if Zn and Cu are connected, Zn acts as anode and undergoes corrosion, whereas Cu acts as cathode.



The reaction at the cathode depends upon the environment.

Acidic environment



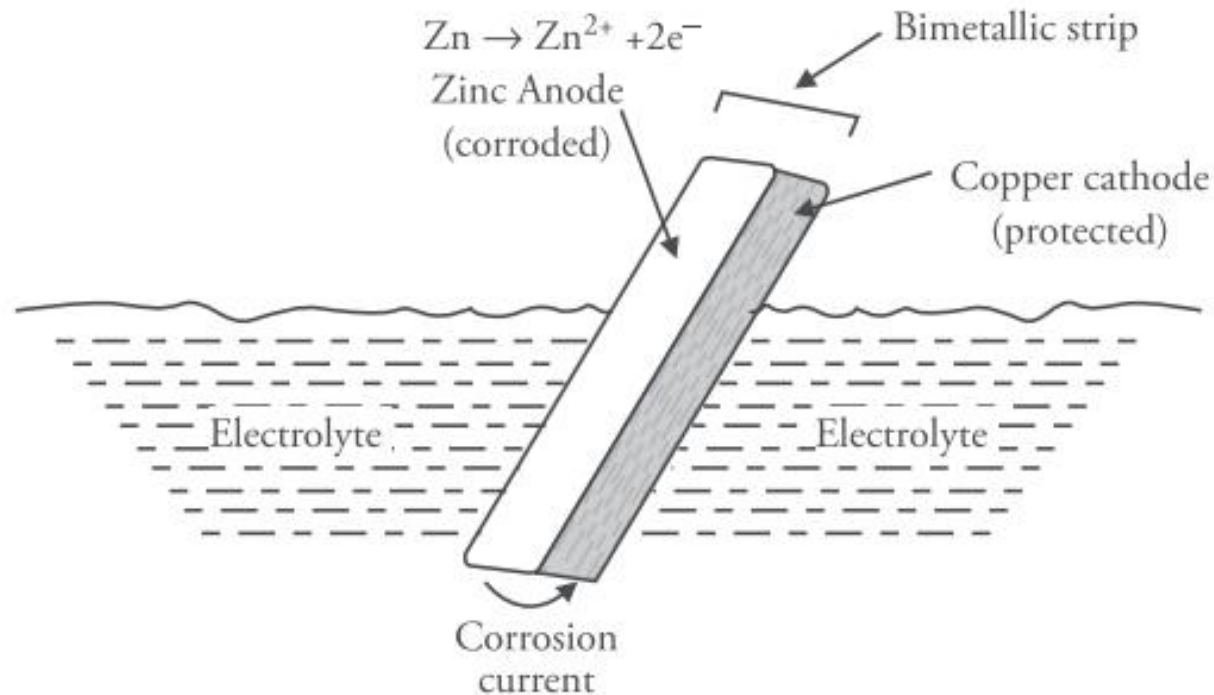
Alkaline or neutral environment



Zn^{2+} and 2OH^{-} ions interact to form $\text{Zn}(\text{OH})_2$. Hence, Zn dissolves and Cu is protected.

The common examples of galvanic corrosion are as follows

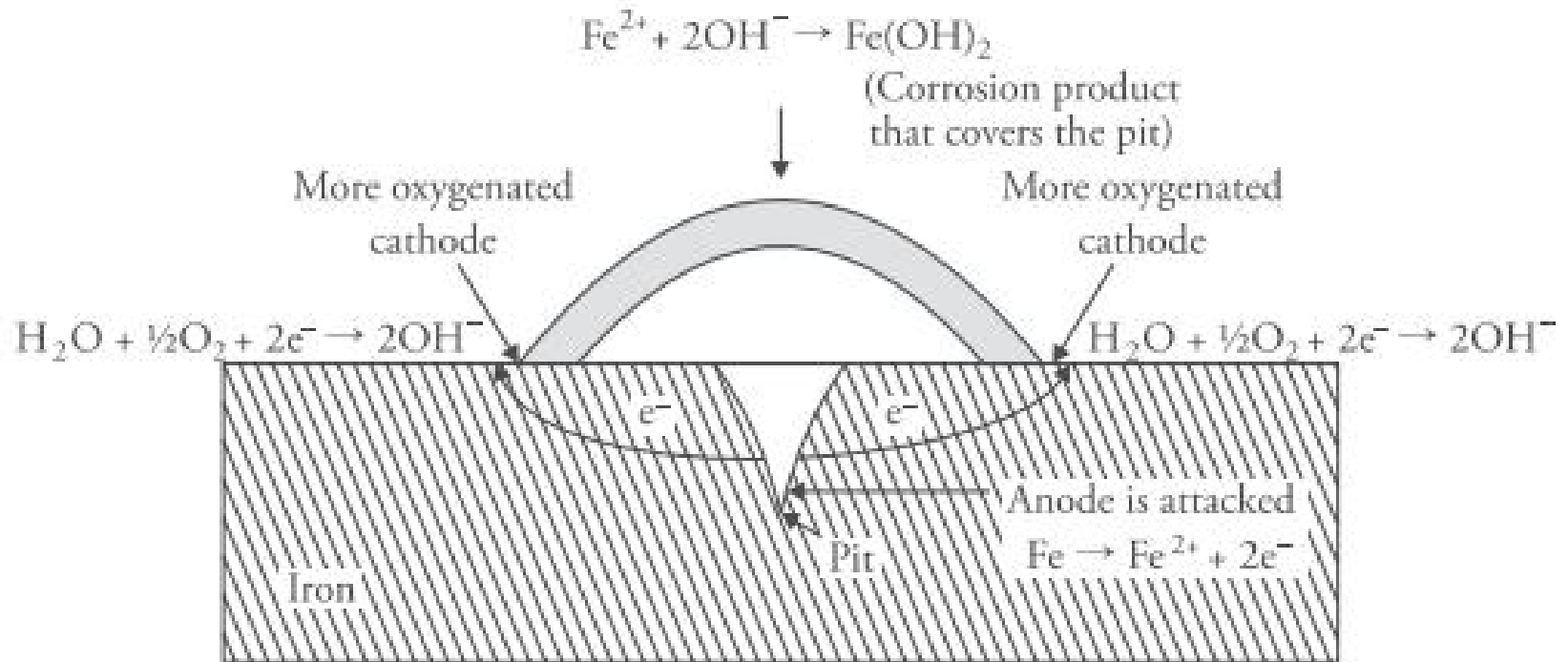
- Use of Cu pipes in conjunction with iron pipes in water distribution system.
- A steel propeller shaft in a bronze bearing.
- Steel screw in brass marine hardware.
- Lead–antimony solder around Cu wire.

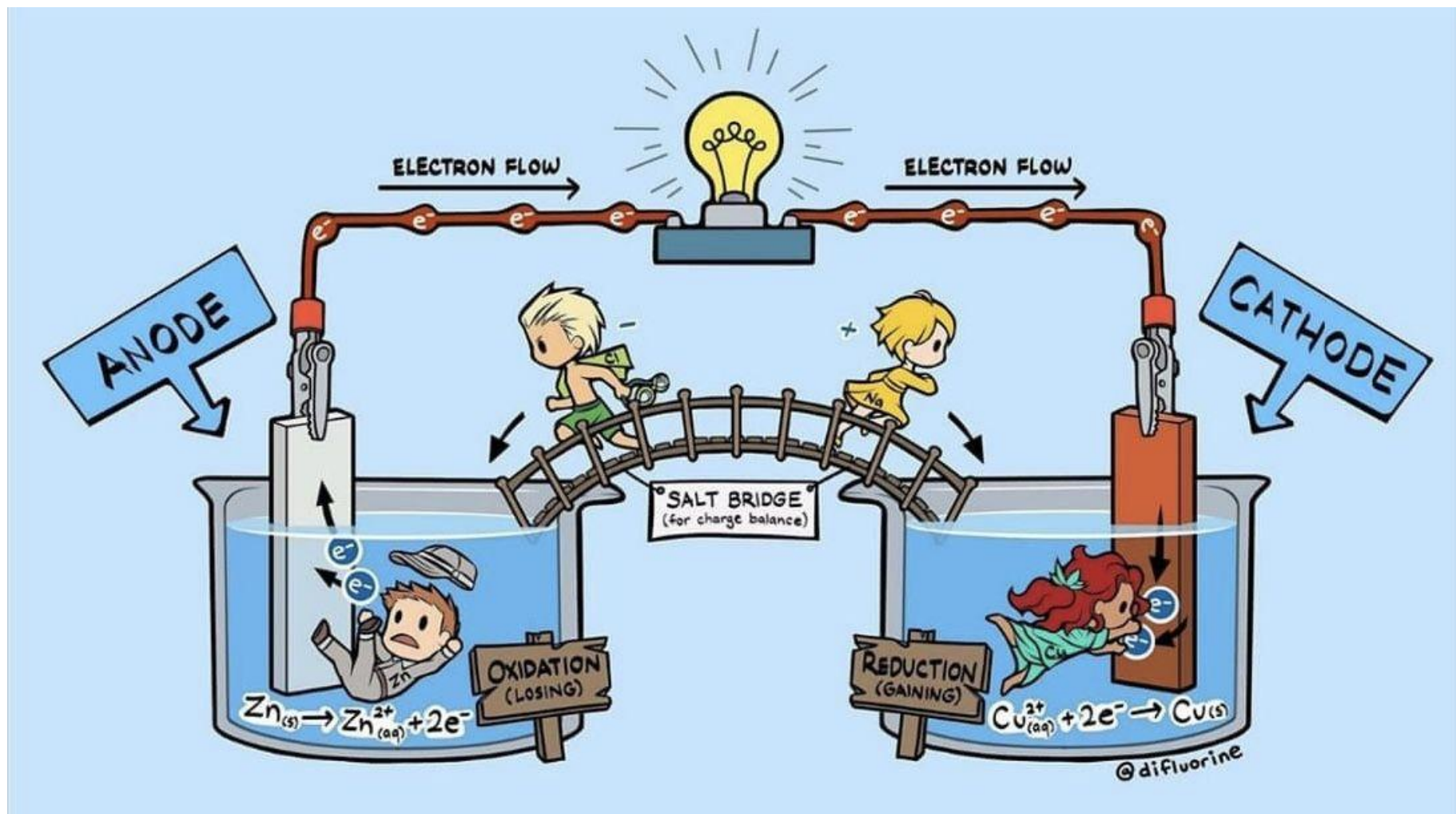


Pitting Corrosion: It is also an example of differential aeration corrosion. It is a localised type of corrosion and occurs in areas of pits, cavities and pinholes that penetrate deeply within the metals (Fig. 3.9). The pit is oxygen deficient and acts as anode, whereas the plane surface is oxygen-rich and acts as cathode. As the area of anode is small the rate of corrosion will be high. Anodic metal dissolves and the pit gradually deepens resulting in the weakening of the metal in these areas. If the pits are small they may be covered by corrosion products. Therefore, it is difficult to detect pitting corrosion till sudden failure of the metal occurs.

Pitting of metal generally occurs because of breakdown or cracking in the protective film on the metal surface at specific points. It may be due to scratches, surface roughness, chemical attack, stresses and strains, etc.

Pitting is common in aluminium alloys, copper alloys, stainless steels and some nickel alloys. Pits are initiated by activating ions like chloride ions. Pits may be shallow or deep. Iron buried in soil generally corrodes by the formation of shallow pits whereas stainless steel immersed in sea water corrodes with the formation of deep pits.





THANK YOU