

ELECTROCHEMISTRY

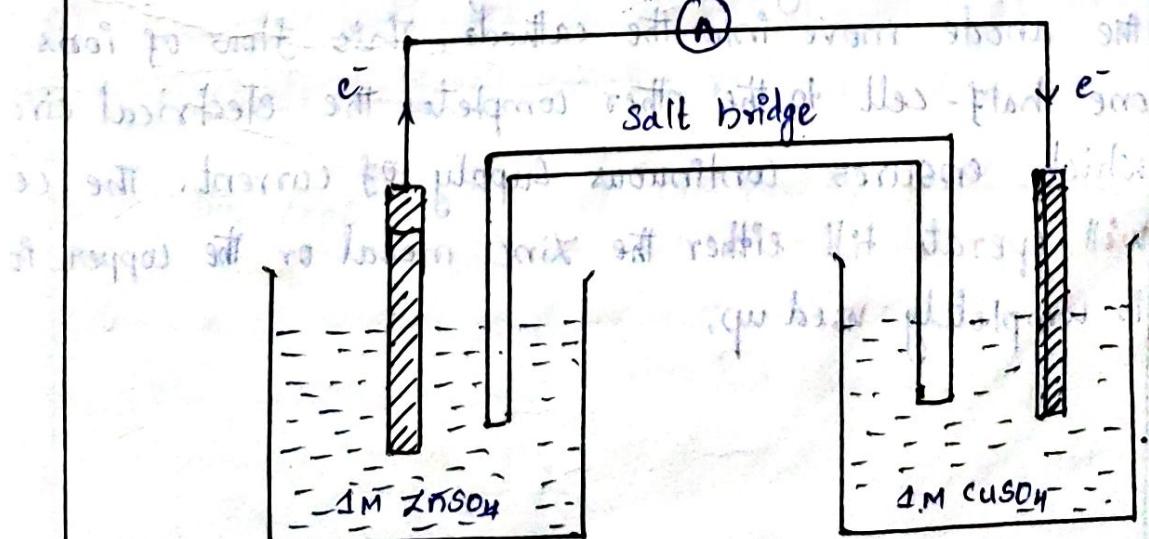
Electrochemical cell

An electrochemical cell is a device used to convert chemical energy into electrical energy. It consists of two electrodes namely anode, cathode and an electrolyte.

In this cell, electrons are transferred in the redox reaction is utilised as a source of producing electrical energy.

Galvanic cell :

In a galvanic cell, a zinc rod is partially immersed in 1M ZnSO_4 solution and a copper rod is partially immersed in 1M CuSO_4 solution. The two solutions are interconnected by a salt bridge. The salt bridge is a U-tube containing saturated KCl and NH_4NO_3 in agar-agar gel. The salt bridge provides electrical contact between two compartments.



Galvanic cell

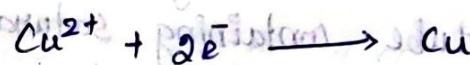
It also helps to maintain electrical neutrality by allowing the migration of ions.

If Zinc and copper rods are connected from outside electrons flow from Zinc to Copper. Since Zinc atoms are oxidized and Copper atoms are reduced. The flow of electrons are indicated by ammeter placed in the circuit.

The oxidation half-reaction that occurs in the anode compartment is



The reduction half-reaction that occurs in the cathode compartment is



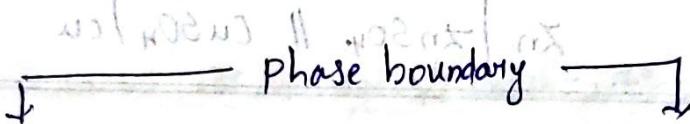
When the cell is set up, electrons flow from Zinc electrode through the wire to the Copper cathode.

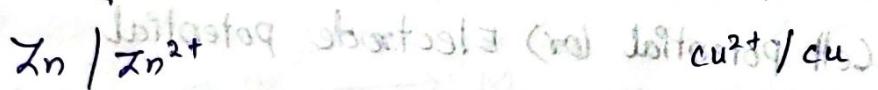
As a result Zinc dissolves to form Zn^{2+} ions in the cell. At the same time SO_4^{2-} ions from the cathode migrate to the anode, through the salt bridge. Likewise, Zn^{2+} ions from the anode move into the cathode. This flow of ions from one half-cell to the other completes the electrical circuit which ensures continuous supply of current. The cell will operate till either the Zinc metal or the Copper ion is completely used up.

Cell Diagram or Representation of a cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. The cell consists of two half-cells. Each half-cell is again made of a metal electrode in contact with metal ions in the solution.

- ① A single vertical line or a semicolon represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are represented

as = 



Anode half cell

Cathode half cell

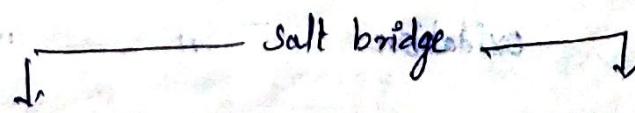


- ② A double vertical line represents the salt bridge, porous partition or any other means permitting ion flow.

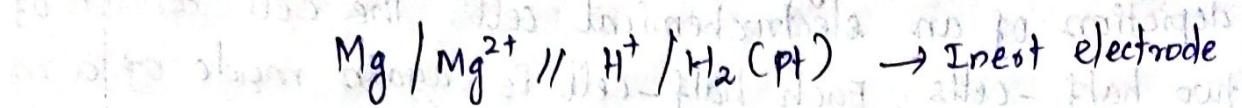
- ③ Anode half-cell is written on the left and cathode half-cell on the right.

The Zinc Copper cell can now be written as

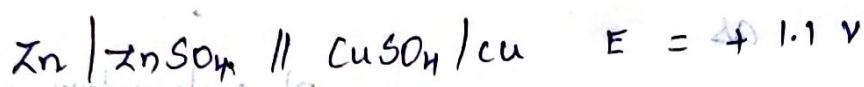
$Zn | Zn^{2+} || Cu^{2+} | Cu$ or $Zn; Zn^{2+} // Cu^{2+}; Cu$



4. The symbol for an inert electrode, like platinum electrode is often enclosed in a bracket.



5. The value of emf of a cell is written on the right of the cell diagram. Thus a Zinc-copper cell has emf 1.1 V and is represented as



Cell Potential (or) Electrode potential

The tendency of an electrode to lose or gain electrons, when it is in contact with its own ions in solution is called electrode potential.

✓ The tendency to gain electrons means the tendency to get reduced. Therefore this tendency is called reduction potential.

✓ The tendency to lose electrons means the tendency to get oxidized. Hence this tendency is called oxidation potential.

example

reduction potential of an electrode is +1.5 V

oxidation potential " " " is -1.5 V

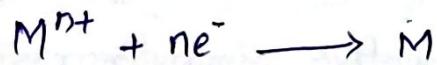
Single Electrode potential

The electrode potential of a single electrode or a half-cell is known as single electrode potential.

It is not possible to determine experimentally the potential of a single electrode. In order to determine it, the electrode whose potential has to be determined is coupled with a standard electrode to form a complete cell. The standard half-cell used for the purpose is standard hydrogen electrode (SHE)

NERNST EQUATION

Consider the following redox reaction



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

$$\Delta G = -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\Delta G^\circ = -RT \ln K + E^\circ = \dots$$

So

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \rightarrow ①$$

Where

$$\Delta G^\circ = \text{standard free energy change.}$$

The decrease in free energy in the reversible reaction is equivalent to the electrical energy.

$$\Delta G^\circ = -nE^\circ F \quad \rightarrow ②$$

Where

E = Electrode potential

E° = Standard electrode potential

F = Faraday (96,500 coulombs)

Comparing equation (1) and (2)

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \rightarrow ③$$

Nernst equation

Since the concentration of the metal is unity, equation ③ becomes

$$-nEF = -nE^\circ F + RT \ln \frac{1}{[M^{n+}]}$$

$$-nEF = -nE^\circ F + RT \ln [M^{n+}] \rightarrow ④$$

Dividing equation ④ by $-nF$, we get

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^\circ_{\text{Red}} + \frac{0.0591}{n} \log [M^{n+}] \rightarrow ⑤$$

$$E = E^\circ_{\text{Oxi}} - \frac{0.0591}{n} \log [M^{n+}] \rightarrow ⑥$$

The equations (5 & 6) are known as Nernst equation for the electrode potential at 25°C .

$$T^\circ \text{E}^\circ = 0 \text{ V}$$

THERMODYNAMICS

Thermodynamics is a branch of science which gives a quantitative treatment of energy changes from one form to another during physical and chemical processes.

Thermo means 'Heat'
dynamics means 'motion'

So Thermodynamics means 'motion of heat'

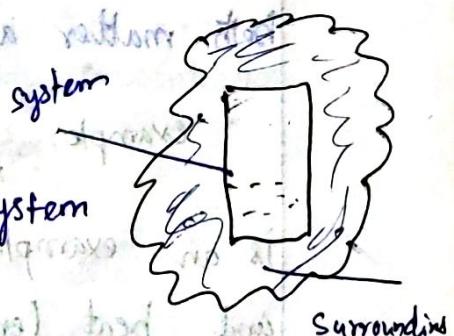
Basic Concepts of Thermodynamics

System

A Thermodynamic system contains quantity of matter enclosed by a boundary which may be real and imaginary.

Surroundings

Everything external to the system is called the surroundings.

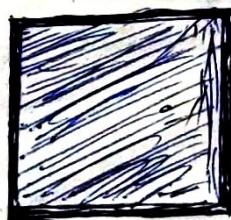


Types of System

1. Isolated System:

An isolated system is one in which there is no interaction between the system and the surroundings i.e. The system does not exchange any matter or energy with its surroundings.

example:



Boiling water in a thermo flask. Due to insulation neither water (matter) nor heat (energy) can be exchanged with its surroundings.

2. closed System

A closed system is one which can transfer energy in the form of heat, work with its surroundings but not matter.

Example: A gas kept in a cylinder fitted with movable piston is an example of closed system.



3. open system

An open system is one which exchanges both matter and energy with its surroundings.

Example: A beaker containing hot water placed on the table is an example of open system. The water vapour (matter) and heat (energy) are transferred to the surroundings through the imaginary boundary.



Properties of a system

The properties of a system can be divided into two classes.

1. Extensive properties:

Extensive properties are those which depend on the amount of the substance present in the system.

Example:

Mass, volume, internal Energy (E), Enthalpy (H)

Entropy (S), Free energy (G)

2. Intensive Properties:

Intensive properties are those which are independent of the amount of the substance present in the system.

example: Temperature, Pressure, Density, concentration,

Surface tension, Viscosity, Refractive Index

example: Boiled water in a beaker at 25°C
Temperature of any drop of water is 25°C

Types of process of a System.

If a system may change from one state to another by path. The path by which this change of state occurs is called a process.

1. Isothermal (or) Constant temperature process

If a system is perfectly conducting to the surroundings and the temperature remains constant throughout the process, it is called isothermal process.

$$\Delta T = 0$$

$$\Delta q \neq 0$$

2. Adiabatic Process

In an adiabatic process, there is no exchange of heat between a system and surroundings.

i.e During an adiabatic process, the working substance is perfectly insulated from the surroundings. (Thermoflask)

$$\boxed{\delta q = 0}$$

- no exchange heat

$$\boxed{dT \neq 0}$$

- change in temperature

Reversible process:

It is a process in which the state of the system is changed infinitesimally slowly so that its direction at any point can be reversed by a small change in any of the thermodynamic variables.

example: Ice melts when a certain amount of heat is absorbed by it. The water so formed can be converted into ice, if the same amount of heat is removed from it. Hence Process is reversible.

Irreversible Process:

It is a process in which the state of system is changed rapidly so that its direction at any point cannot be reversed by a small change in any of the thermodynamic variables.

example: All naturally occurring processes are spontaneous or irreversible.

Raining, water falling from hills

Falling Mango from tree etc.

ΔH (H) refers to the standard heat (Q) required

Process	Condition
Adiabatic	$Q=0$
Isothermal	$dT=0$
Isobaric	$dP=0$
Isochoric	$dV=0$
cyclic	$dE=0, dH=0$ $dP=0, dV=0$ $dT=0$

Isobaric process

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

$$\boxed{dP = 0}$$

Left word set

$$dQ + \delta H = H$$

Isochoric process

An isochoric process is defined as the one in which the volume of system remains constant during its change from initial to final state.

$$\boxed{dV = 0}$$

similar factors

$$dQ - P \delta V = \delta U$$

$$\delta U = Q - PV$$

$$\boxed{Q = \delta U + PV}$$

$$\boxed{\delta U = Q - PV}$$

For adiabatic (Q=0) processes we consider with same condition to avoid a confusion (PV) equals to

ENTHALPY (OR) Heat content of a System (H)

Enthalpy is defined as the sum of internal Energy (E) and pressure-volume change (work done) of a system under particular set of conditions

$$H = E + PV$$

Enthalpy change (ΔH)

It is the difference in the enthalpy of initial and final stages of the system

$$\Delta H = H_{\text{final}} - H_{\text{Initial}}$$

$$= H_2 - H_1$$

We know that

$$H = E + PV$$

$$\Delta H = (E_2 + PV_2) - (E_1 + PV_1)$$

$$= (E_2 - E_1) + P(V_2 - PV_1)$$

$$\Delta H = \Delta E + P\Delta V$$

At constant volume

$$V = 0$$

$$\Delta H = \Delta E$$

$$\Delta E = q$$

$$q_p = \Delta H$$

The change in enthalpy (ΔH) is equal to the quantity heat changes (q_p) accompanying a process at constant pressure

Entropy

Entropy is a measure of degree of disorder (or randomness) in the system. It is also considered as a measure of unavailable form of energy.

Mathematical expression for Entropy

The change in entropy is equal to the ratio of heat change to the temperature at which heat change occurs in reversible cyclic process.

$$\Delta S = \frac{q_{rev}}{T} \quad \text{units of } \text{cal deg}^{-1} \text{ (or) } \text{J K}^{-1} \text{ mol}^{-1}$$

In isothermal reversible

$$\begin{aligned} \text{Total change in entropy of the system} &= \Delta S \\ \text{Change in entropy of the system} &= \Delta S_{\text{System}} \\ \text{Change in entropy of the surroundings} &= \Delta S_{\text{Surroundings}} \\ q_{rev} = \Delta S T & \quad \frac{q}{T} = \Delta S_{\text{System}} \\ \text{we get on } ② = i & \left(\frac{q}{T} \right) + \left(-\frac{q}{T} \right) \end{aligned}$$

$$\Delta S_{\text{Total}} = 0$$

i.e., Entropy change in a reversible isothermal process is zero. In other word the entropy remains constant during a reversible process.

Entropy change in irreversible (Spontaneous) process.

Let the system be at higher temperature T_1 , and its surroundings at lower temperature T_2 . Consider a quantity of heat $-q$ passes irreversibly from system to surroundings.

$$\text{Net entropy change in process (}\Delta S_{\text{net}}\text{)} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2}$$

$$= q \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$= q \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

$$\text{Decrease in entropy of system} = -\frac{q}{T_1} \quad (\Delta S_{\text{sys}})$$

$$T_1 > T_2$$

$$\text{Increase in entropy of surroundings} = +\frac{q}{T_2} \quad (\Delta S_{\text{sur}}) \quad \Delta S_{\text{sur}} > 0$$

GIBBS - HELMHOLTS EQUATION (or) Relation between ΔG & ΔH

(Let) Consider the following relation

$$G = H - TS \quad (\text{Gibbs free energy}) \rightarrow ①$$

$$H = E + PV \quad (\text{Enthalpy}) \rightarrow ②$$

Substituting eqn ② in ①

$$G = E + PV - TS \rightarrow ③$$

For infinitesimal change

$$dG = dE + pdv + vdp - Tds - sdt \rightarrow ④$$

According to I & II law of thermodynamics

$$④ \leftarrow dE = dq + pdv \quad (\text{I law})$$

$$dq = Tds \quad (\text{II law})$$

$$④ \leftarrow dE = Tds - pdv \rightarrow ⑤$$

Substituting eqn ⑤ in ④

$$dG = Tds - pdv + pdv + vdp - Tds - sdt$$

$$dG = vdp - sdt$$

$$VdP - \chi_{\text{ext}} dW = \Delta A -$$

At constant (P) $dp = 0$ then eqn ⑥ becomes

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (\text{or}) \quad dG = \text{CONSTANT} \rightarrow ⑦$$

Substituting eqn ⑦ in eqn ① and after the similar

$$H = G + T \left(\frac{\partial G}{\partial T}\right)_P \quad (\text{Gibbs-Helmholtz Equation})$$

(iv)

$$H = G - T \left(\frac{\partial G}{\partial T}\right)_P$$

For a change from state 1 to 2, variables such as free energy (G) and Enthalpy (H) undergoes changes, then the above equation can be written as

$$\Delta G = AH - \left(\frac{\partial (AG)}{\partial T}\right)_P$$

(v)

$$\Delta H = \Delta G - T \left(\frac{\partial (\Delta G)}{\partial T}\right)_P$$

Similarly

$$\Delta A = \Delta E - T \left(\frac{\partial (\Delta E)}{\partial T}\right)_V$$

may be derived.

It is also important to note that

it builds up on the principle of pair approximation

and off the off-site pair hopping in magnetic compounds having two-fold site exchange

Corrosion

Definition

Corrosion is defined as the spontaneous process of degradation of metallic constructions in the course of their chemical, bio-chemical or electrochemical interaction with the environment.

Example

Rusting of iron

When a piece of iron is exposed to atmospheric conditions, a layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface.

When copper is exposed to moist-air containing CO_2 , a green film of basic carbonate $[\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2]$ is formed on the surface of copper.

Classification of Corrosion

Based on the mechanism of corrosion, it is broadly classified into two types. They are

(1) Dry corrosion (or) Chemical corrosion

(2) Wet corrosion (or) Electrochemical corrosion.

Dry corrosion (or) Chemical corrosion

Dry (or) chemical corrosion takes place due to the direct chemical action of atmospheric gases, such as oxygen, halogen sulphide, sulphur dioxide, nitrogen (or) oxygen, halogen sulphide, sulphur dioxide, nitrogen

anhydrous inorganic liquid with metal surfaces.

Types of Dry corrosion

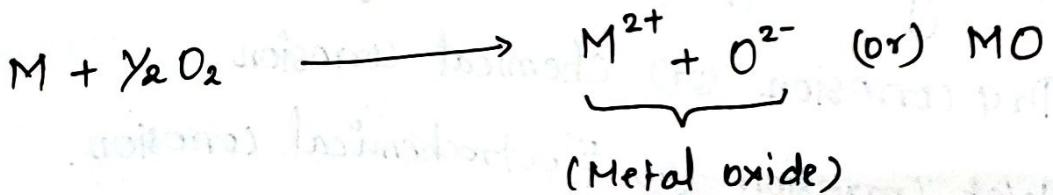
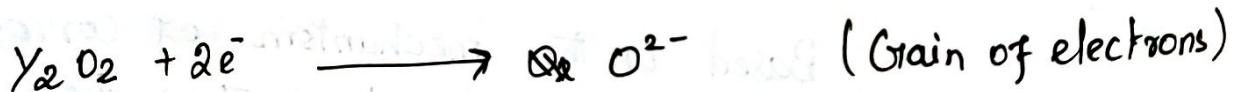
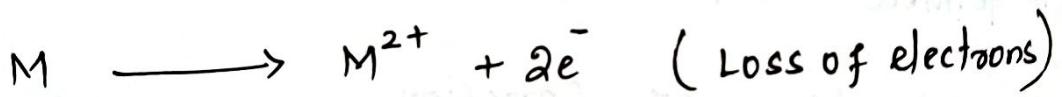
Dry corrosion is further classified into

- (a) Oxidation corrosion
- (b) Corrosion by other gases
- (c) Liquid metal corrosion.

(a) Oxidation corrosion

When oxygen directly attacks the metal surfaces at low (or) at high temperatures, oxidation corrosion takes place. This type of corrosion usually occurs in the absence of moisture.

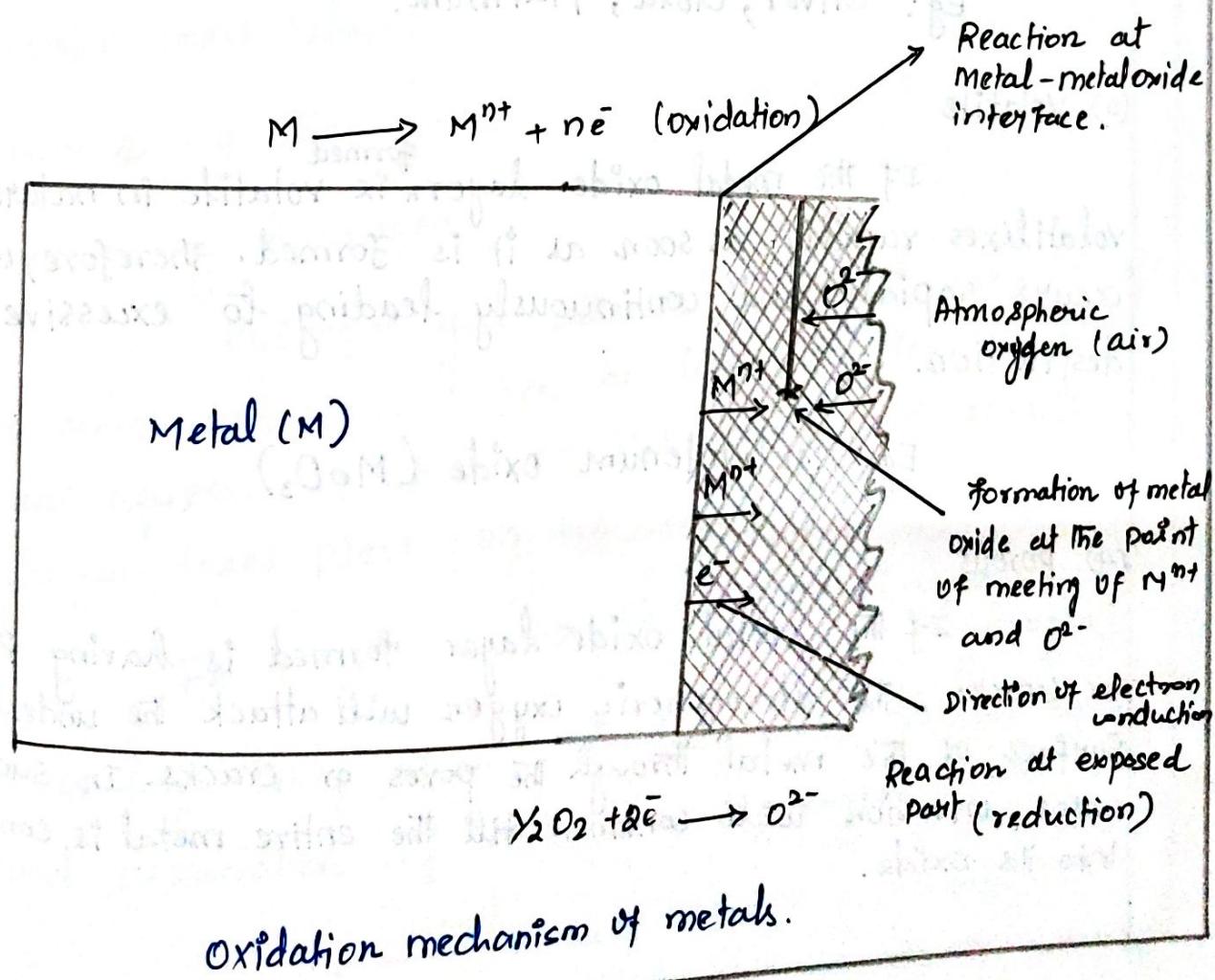
The following reactions takes place during oxidation corrosion.



Mechanism

* Oxygen attacks the surface of the metal and oxidation takes place. This results in the formation of metal oxide scale.

- * The metal oxide scale formed on the metal surface acts as a barrier and prevents further oxidation.
- * If oxidation has to continue, either metal ions must diffuse outward through metal oxide barrier or oxide ions must diffuse inward through the barrier.
- * Though both transfers occur, the outward diffusion of the metal ions is more rapid than the inward diffusion of oxide ions.
- * This may be accounted for by the higher mobility and smaller size of metal ions when compared to oxide ions.



Nature of the metal oxide

The nature of the metal oxide formed is the deciding factor for further oxidation.

(1) Stable

If the metal oxide layer formed is stable, fine-grained, tightly adhering and impervious in nature, further oxidation corrosion is prevented.

Eg: Oxide films on Al, Sn, Pb, Cu, Pt etc.

(2) Unstable

The oxide film formed decomposes back into metal and oxygen and hence corrosion is not possible in such a case.

Eg: Silver, Gold, platinum.

(3) Volatile

If the metal oxide layer ^{formed} is volatile in nature, it volatilizes rapidly as soon as it is formed. Therefore, corrosion occurs rapidly and continuously leading to excessive destruction.

Eg: Molybdenum oxide (MoO_3)

(4) Porous

If the metal oxide layer formed is having pores or cracks, the atmospheric oxygen will attack the underlying surface of the metal through the pores or cracks. In such cases, corrosion will continue till the entire metal is converted into its oxide.

Pilling - Bedworth Rule

According to this rule "an oxide is protective and non-porous, if the volume of the oxide is greater than the volume of the metal from which it is formed.

Eg: If the Aluminium oxide layer volume is greater than the volume of Al corrosion will not take place.

On the other hand, the metal oxide film is non-protective and highly porous, if the volume of the metal oxide is lower than the volume of the metal.

Eg: Volume of oxide layer of alkaline and alkali earth metals is less than the volume of the metals. Hence corrosion takes place.

corrosion by other gases

corrosion by hydrogen

Hydrogen gas attacks the metal surface and causes corrosion. When an iron piece is exposed to an aqueous solution of H_2S evolution of atomic hydrogen takes place on the iron surface.



At high temp atomic hydrogen is formed by the thermal dissociation of molecular hydrogen.



This atomic hydrogen diffuses into the metal and collects in the voids. These it recombines to form molecular hydrogen.



The formation of hydrogen results in increase in the pressure of hydrogen inside the voids and causes blisters and fissures. This process is termed as 'hydrogen embrittlement'.

When steel is exposed to this environment the atomic hydrogen readily combines with carbon of steel and produces methane gas.



Collection of these gases in the voids develop very high pressure which causes cracking. Thus the process of decrease in carbon content in steel is called as decarburisation of steel.

Wet or Electrochemical corrosion:

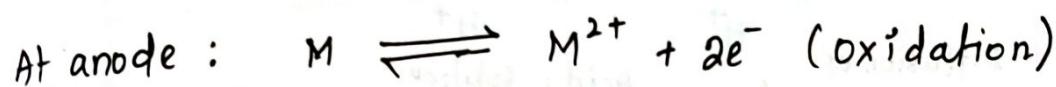
Electrochemical corrosion involves:

- (i) The formation of anodic and cathodic areas or parts in contact with each other
- (ii) Presence of conducting medium.
- (iii) formation of corrosion product somewhere between anodic and cathodic areas. This involves flow of

electron-current between the anodic and cathodic areas.

Mechanism of wet or electrochemical corrosion

In electrochemical corrosion, electron-current flows between the anodic and cathodic regions. At the anode, the dissolution of metal into corresponding metallic ions takes place. The electrons liberated during this process is consumed at the cathode.



The consumption of electrons by cathodic region may take place by either of the following types.

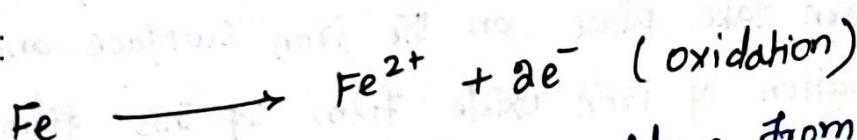
(a) Evolution of hydrogen

(b) Absorption of oxygen

a) Evolution of hydrogen.

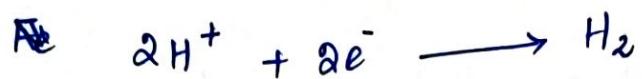
This type of corrosion occurs in acidic environments. Consider the corrosion process in an iron metal. At anodic region, the iron is dissolved into ferrous ions, where electrons are liberated.

At anode:



These liberated electrons flow from anode to cathode. At cathode, H^+ ions are liberated as hydrogen gas.

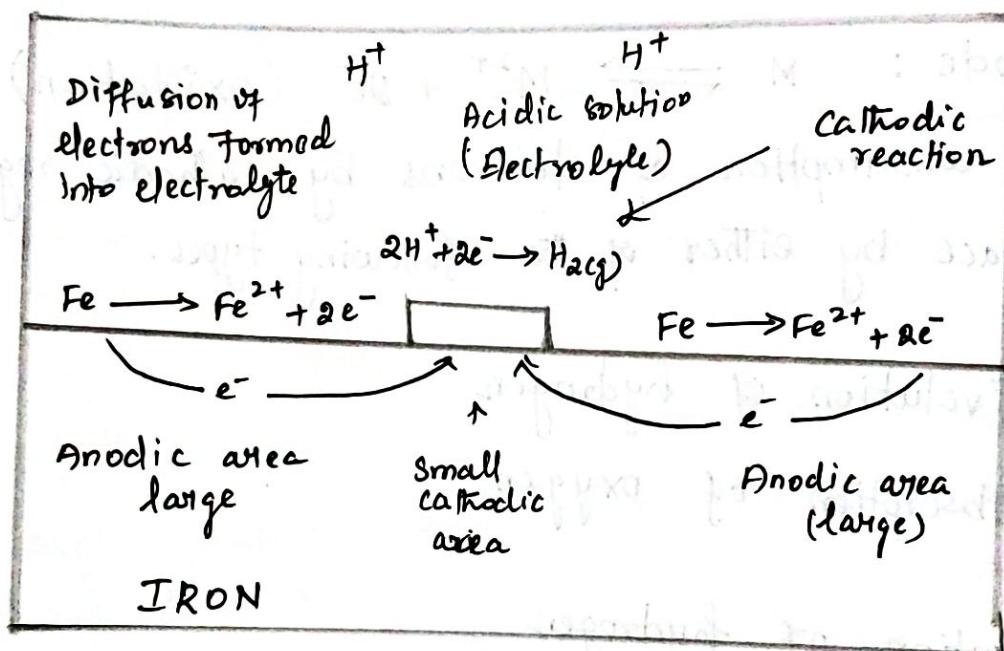
At Cathode:



The overall reaction is



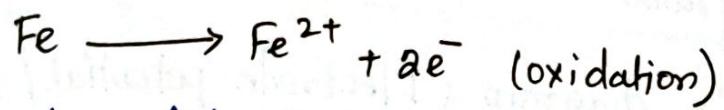
This type of corrosion takes place in all metals above ~~in~~ the hydrogen in the electrochemical series.



b) Absorption of oxygen

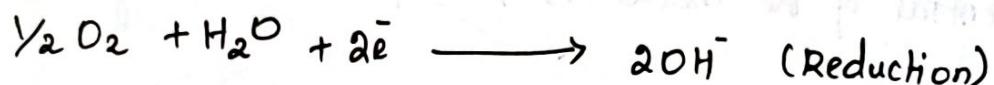
This type of corrosion takes place in neutral environments. A best example of this kind of corrosion is rusting of iron. In the presence of atmospheric oxygen, corrosion takes place on the iron surface and there is formation of iron oxide film. If this film develops some cracks, anodic areas are created on the surface while other parts act as cathodes.

Anode



The liberated electrons flow from anodic to cathodic areas through the metal and accepted by the dissolved oxygen.

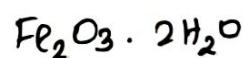
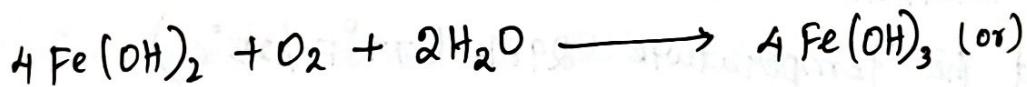
cathode



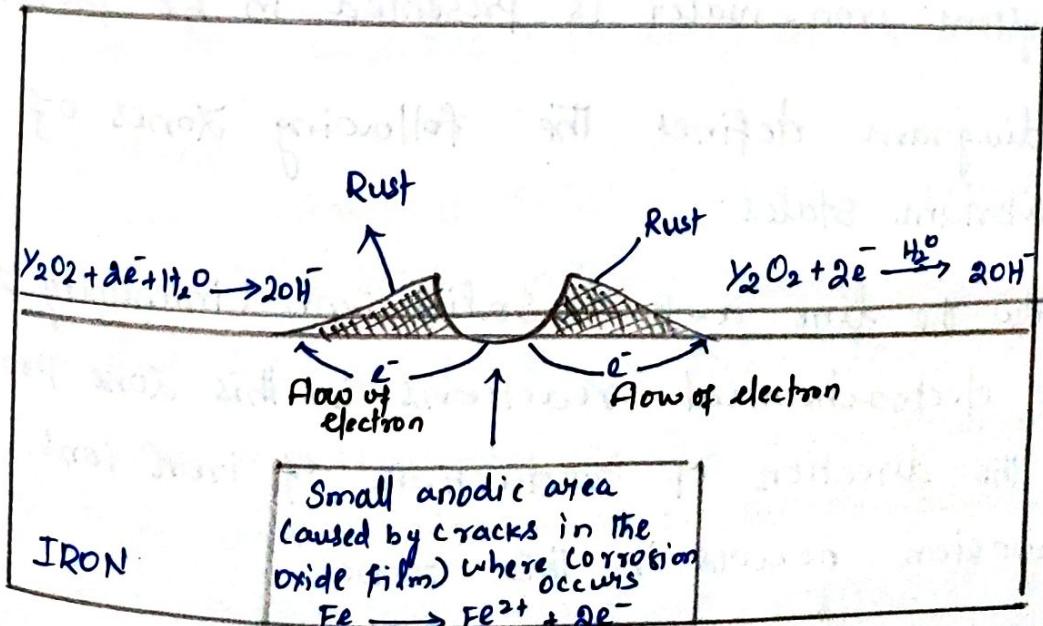
The Fe^{2+} ions and OH^- ions diffuse and react to form Fe(OH)_2



If enough oxygen is present ferrous hydroxide is oxidized to ferric hydroxide



Rust.



Pourbaix diagrams

Pourbaix diagram (Electrode potential / pH diagram) is a graphical presentation of the thermodynamic equilibrium states of a metal - electrolyte system.

Pourbaix diagrams are plotted in the axes Electrode potential of the metal vs pH of the electrolyte.

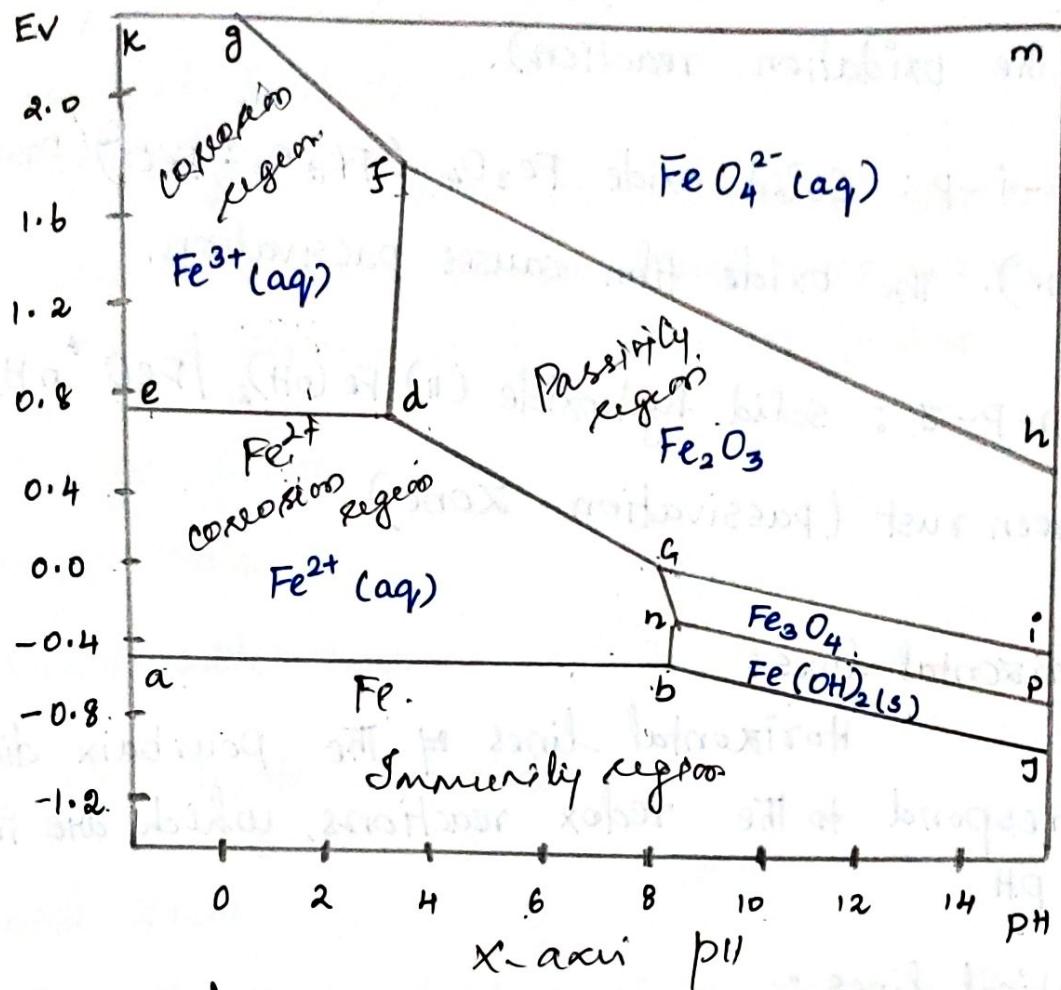
Pourbaix diagrams allow to determine the corrosion behaviour of metal in water solutions i.e. the direction of electrochemical processes and the equilibrium state of the metal at a certain electrode potential in a water solution at certain value of pH.

Normally the Pourbaix diagrams are built for the water solutions with the concentrations of metal ions 10^{-5} M and at the temperature 298 K (77°F / 25°C)

An example of a Pourbaix diagram for the system iron - water is presented in the picture.

The diagram defines the following zones of the equilibrium states:

- * below the line a-b-j solid iron (immunity zone)
The electrochemical reactions in this zone proceed in the direction of reduction of iron ions. No corrosion occurs in this zone.



* a-b-n-c-d-e :

Aqueous solution of ion Fe^{2+} (corrosion zone)
Metallic iron oxidizes in this zone

* e-d-f-g-k :

Aqueous solution of ion Fe^{3+} (corrosion zone)
Metallic iron oxidizes (corrodes) in this zone.

* h-f-g-m :

Aqueous solution of ion FeO_4^{2-} (corrosion zone).

* c-d-f-h-i : Solid Ferrus oxide Fe_2O_3 (passive zone)

Iron oxidizes (corrodes) in this zone however the

resulted oxide film depress the oxidation process

causing passivation (corrosion protection of the metal)

due to formation of a film of a solid product of the oxidation reaction).

n-c-i-p : Solid oxide Fe_3O_4 ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$) (Passivation zone). The oxide film causes passivation.

b-n-p-j : solid hydroxide (II) $\text{Fe}(\text{OH})_2$ / $\text{FeO} \cdot n\text{H}_2\text{O}$ / green rust (passivation zone)

Horizontal lines :

Horizontal lines of the Pourbaix diagrams correspond to the redox reactions, which are independent of pH.

Vertical lines :

Vertical lines of the Pourbaix diagrams correspond to the non-redox reactions (electrons are not involved), which are dependent on pH.

Diagonal lines :

Diagonal lines of the Pourbaix diagrams correspond to the redox reactions, which are dependent on pH.