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B.Tech Chemistry
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SRM
INSTITUTE OF SCIENCE & TECHNOLOGY
(Deemed to be University u/s 3 of UGC Act, 1956)

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Module: 4
Thermochemistry

Chapter Outline:
Thermodynamic functions

- Internal energy,
- Helmholtz free energy,
- Enthalpy, (Definition, expression & explanation)
- Entropy and free energy

Thermochemistry

- **Thermochemistry** is the study of the heat energy which is associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling.

- Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its a surroundings.

- Thermochemistry is useful in predicting reactant and product quantities throughout the course of a given reaction.

- In combination with entropy determinations, it is also used to predict whether a reaction is spontaneous or non-spontaneous, favorable or unfavorable.

Terms used in Thermodynamic

Energy: The capacity to do work or to produce heat

Law of conservation of Energy:

- Energy can be converted from one form to another but can be neither created nor destroyed. The energy of the universe is constant.

The two types of Energy:

- **Potential Energy**: Energy due to position or composition- can be converted to work .
- **Kinetic energy:** Energy due to the motion of the object and depends on the mass of the object m and its velocity v, K.E= ½ mv2
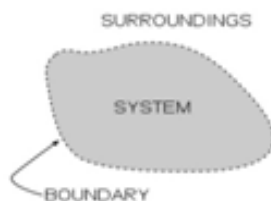
System

- May be defined as the part of universe selected for thermodynamic consideration i.e,, to study the effect of temperature , pressure etc.
- It may be also defied as specified part of universe in which energy changes are taking place

Surrounding

- The remain portion of universe excluding the system is called surrounding

  Universe= System + surrounding

- The system and surrounding can be separated by real and imaginary boundary

Types of System

Open System:
Here mass and energy can be exchanged with surrounding
ex: If some water is kept in open vessel or hot tea in open cup

Closed System: In a closed system, there is only the exchange of energy with surrounding, no exchange of mass takes place.

For example. If water is placed in closed metallic vessel or hot tea placed in closed tea pot.

isolated system is one that cannot exchange either matter or energy with its surroundings.

For ex: water placed in a vessel which is closed as well as insulated or tea placed in a thermos flask.

Intensive properties and Extensive properties

Intensive properties
- Properties of the system which depend only on the nature of matter but not on the quantity of matter are called Intensive properties, e.g., pressure, temperature, specific heat, etc

Extensive Properties
- Properties of the system which are dependent on the quantity of matter are called extensive properties, e.g., internal energy, volume, enthalpy, etc
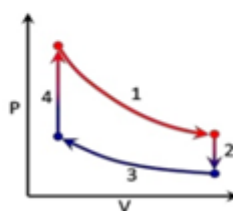
State of System
    When microscopic properties have definite value, the conditions of existence of the system is known as state of system.

State functions When values of a system is independent of path followed and depend only on initial and final state, it is known as state function,e.g., $\Delta U, \Delta H, \Delta G$ etc.

Path functions These depend upon the path followed, e.g., work, heat, etc.

Process

- When state of system changes then process is said to occur.
- The first and last sate of process are called initial and final state respectively.
- Process gives us the path by which system changes from one state to other.
- There are certain processes in which particular state variable is kept constant .

Types of Process

Isothermal Process:

- It is defined as the process in which temperature of system remains constant.
- Heat can flow from system to surrounding and vice versa in order to keep the temperature constant .
- $(dT = 0, \Delta U = 0)$.
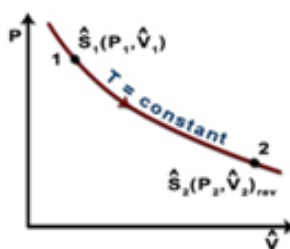
Adiabatic Process: $(\Delta q = 0)$

- The system does not exchange heat with the surrounding
- System is completely insulate from surrounding

Isochoric Process: $(\Delta V = 0)$.

- Volume of system remains constant during the process

Isobaric process: $(\Delta p = 0)$.

- Here pressure of the system remains constant during the process

Cyclic Process $\Delta U_{cyclic} = 0; \Delta H_{cyclic} = 0$

- Here the system undergoes series of changes and finally returns to its initial state

Reversible Process:

- **Reversible process** A process that follows the reversible path, i.e., the process which occurs in infinite number of steps in this Way that the equilibrium conditions are maintained at each step, and the process can be reversed by infinitesimal change in the state of functions

Irreversible process

- **Irreversible process** The process which cannot be reversed and amount of energy increases. All natural processes are Irreversible.

Spontaneous process

- It may also be defined as the process which can take place by itself or initiation

Which take place by itself

- Evaporation of water in open vessel
- Dissolution of salt in water
- Flow of w

Non spontaneous process

- It is the process which cannot take place by itself or imitation
- Ex: flow of heat from cold body to hot body
- ater down a hill

Internal energy

- It is the total energy within the substance. It is the sum of many types of energies like vibrational energy, translational energy. etc. It is a extensive property and state function.
- Its absolute value cannot be determined but experimentally change in internal energy (Δ) can be determined by
- $\Delta U = U_2 - U_1$ or $\Sigma U_p - \Sigma U_R$
- For exothermic process, ΔU = -ve, whereas for endothermic process ΔU = +ve
- U depends on temperature, pressure, volume and quantity of matter.

Change in internal Energy

- The change in internal energy in a chemical reaction is the difference in the internal energies of the product and the reactants.

$$\Delta E = E(Product) - E (Reactant)$$
$$= Ep-Er$$

Change in internal energy

Heat of Reactants :

The difference between the heat contents of the products and the reactants

Mathematically this function is defined by the relation

$$H = E + PV$$

like internal energy, the absolute value of entropy cannot be determined. Therefore change in entropy (ΔH) determined from 1st law of thermodynamics

$$q = \Delta E + P\Delta V \text{ (at constant pressure)}$$
$$= (E_2 - E_1) + P(V_2 - V_1)$$
$$= E_2 - E_1 + PV_2 - PV_1$$
$$= (E_2 + PV_2) - (E_1 + PV_1)$$
$$= H_2 - H_1 = \Delta H$$

Therefore, $q = \Delta H$ { since $\Delta H = H_2 - H_1$}

Since , the expression of gas is carried at constant pressure (P), then at the work done by the system

$$W = P\Delta V \text{ { from eq, } q = \Delta E + W \text{ can be written as}}$$
$$q = \Delta E + W$$
$$= \Delta E + P\Delta V \text{ (or) } \Delta E = q - P\Delta V$$

Enthalpy (H)

It is the sum of internal energy and pV-energy of the system. It is a state function and extensive property. Mathematically,

$$H = U + pV$$

Like U. absolute value of H also cannot be known, ΔH is determined experimentally.

$$\Delta H = H_2 - H_1$$
$$\text{or } \Sigma H_p = \Sigma H_R$$

For exothermic reaction (the reaction in which heat is evolved), $\Delta H = -ve$

whereas for endothermic reaction (the reaction in which heat is absorbed), $\Delta H = +ve$.

Relationship between ΔH and ΔU

$$\Delta H = \Delta U + \Delta p \, \Delta V$$
$$\text{or } \Delta H = \Delta U + \Delta n_{(g)} RT$$

Here, $\Delta n_{(g)}$ = change in the number of gas moles.

Change in Enthalpy

• It is the difference in the enthalpies of the product and the reactants
• $\Delta H = H(product) - H(reactant)$

Entropy (S)

- Its is a measure of the randomness or disorder of the system
- The greater of the randomness, the greater the entropy
- Entropy of a crystalline substance is minimum in the solid state and maximum in the gaseous state
- Its depends on temperature and increase with increasing temperature
- The change in entropy is equal to heat absorbed isothermally and reversibly during a process divided by absolute temperature at which heat is adsorbed.
- Units : $jK^{-1} mol^{-1}$
- The change in entropy during a process is mathematically given as

$$\Delta_r S° = \Sigma S° \text{ (products)} - \Sigma S° \text{ (reactants)}$$
$$= q_{rev} / T = \Delta H / T$$

Where, q_{rev} heat absorbed by the system in reversible manner, T = temperature

- $\Delta S > 0$, Increase in randomness, heat is absorbed
- $\Delta S < 0$, Decrease in randomness, heat is evolved.
- Entropy of even elementary substances are not zero.
- Entropy change of an ideal gas is given by
- $\Delta S = {_n}C_V \ln (T_2 / T_1) + nR \ln (V_2 / V_1)$

- **Gibbs Energy or Gibbs Free Energy**
- It is the energy available for a system at some conditions and by which useful work can be done. It is a state function and extensive property.

Mathematically,

$$G = H - TS$$

Change in Gibbs energy during the process is given by Gibbs Helmholtz equation.

$$(\Delta G = G_2 - G_1 = \Delta H - T\Delta S)$$

where, ΔG = Gibbs free energy

H = enthalpy of system

TS = random energy

$\Delta G_{system} = - T\Delta S_{total}$

The Gibbs energy criterion of spontaneity

$\Delta G > 0$, process is non-spontaneous

$\Delta G < 0$, 0, process is spontaneous

$\Delta G = 0$, process is in equilibrium state

- **Standard Free Energy Change (ΔG)**
- It is the change in free energy which takes places when the reactants are converted into products at the standard states, i.e., (1 atm and 298 K)
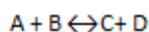
$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = \sum \Delta G_f° \ (product) - \sum \Delta G_f° \ (reactant)$$

where, $\Delta G°_f$ = standard energy of formation

Standard energy of formation of all free elements is zero.

Gibbs Energy Change and Equilibrium

Criterion for equilibrium,

$$A + B \leftrightarrow C + D$$

$$\Delta G = 0$$

Now relation, $\Delta G = \Delta G° + RT\ln Q$

$0 = \Delta G° + RT\ln K$ or $\Delta G° = -RT\ln Q$

$\Delta G° = -2.303 \ RT\ln K$

W.K.T $\Delta G° = \Delta H° - T\Delta S° = -RT\ln K$

Relation between ΔG° and EMF of the Cell

- $\Delta G° = -nFE°_{cell}$
- Where, n = number of electron lost or gained, F = Faraday or 96500 C
- $E°_{cell}$ = standard electrode potential

Laws of Thermodynamic

There are four laws of thermodynamics

- Zeroth law of thermodynamics
- 1st law of thermodynamics
- 2nd law of thermodynamics
- 3rd law of thermodynamics

Zeroth law of thermodynamics or law of thermal equilibrium

- When two bodies A and B are separately in thermal equilibrium with a third body, they in turn are in equilibrium with each other (or)
- The law states that if the two systems are in thermal equilibrium with a third system then they are also in thermal equilibrium with each other. Temperature is used here to know, the system is in thermal equilibrium or not.

First Law of thermodynamics

Energy can neither be created nor destroyed although it can be converted from one form to the other.

Mathematically,

$$\Delta U = q + W$$

where, ΔU = internal energy change

q = heat added to system

W = work added to system

Sign convention

(i) q is + ve = heat is supplied to the system

(ii) q is – ve = heat is lost by the system

(iii) W is + ve = work done on the system

(iv) W is – ve = work done by the system

Second Law of thermodynamics

- The entropy of the universe is always Increasing in the course of every spontaneous or natural change. Or
- All spontaneous processes or natural change are thermodynamically irreversible without the help of an external work. i.e., heat cannot flow itself from a colder to hotter body.
- In an non isolated system the total energy of both the system and surrounding must increase or must be positive
- The total entropy of the universe must tend to increase in spontaneous process

$$\Delta S(total) = \Delta S(system) + \Delta S\ (surrounding)$$

Third Law of thermodynamics

- The entropy of all perfectly crystalline solids may be taken as zero at the absolute temperature
- At absolute zero a perfectly crystalline solid has a perfect order of its constituent particle i.e. there is no disorder at all. Hence absolute entropy is taken as zero

- ## ELECTROCHEMISTRY
  Electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

  ### Electrochemical cell
  An electrochemical cell is a device that produces an electric current from energy released by a spontaneous redox reaction. This kind of cell includes the galvanic, or voltaic cell.

  Electrochemical cells have two conductive electrodes, called the anode and the cathode. The anode is defined as the electrode where oxidation occurs. The cathode is the electrode where reduction takes place

  ## TYPES
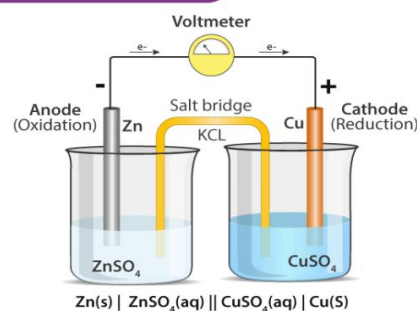 Electrochemical Cells are of two types:
  Galvanic Cells :
  Converts chemical energy into electrical energy
  Electrolytic Cells:
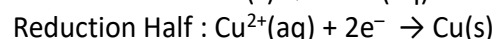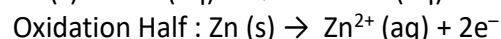   Converts electrical energy into chemical energy.

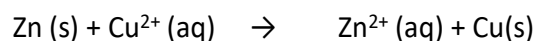## GALVANIC CELL:

Cell energy is extracted from a spontaneous chemical process or reaction and it is converted to electric current.

For example, Daniell Cell is a Galvanic Cell in which Zinc and Copper are used for the redox reaction to take place.

$$Zn \ (s) + Cu^{2+} \ (aq) \quad \rightarrow \quad Zn^{2+} \ (aq) + Cu(s)$$
Oxidation Half : $Zn \ (s) \rightarrow Zn^{2+} \ (aq) + 2e^{-}$
Reduction Half : $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Zn is the reducing agent and Cu^{2+} is the oxidizing agent. The half cells are also known as Electrodes. The oxidation half is known as Anode and the reduction half is called Cathode. Electrons flow from anode to cathode in the external circuit. Anode is assigned negative polarity and cathode is assigned positive polarity. In Daniell Cell, Zn acts as the anode and Cu acts as the cathode.

ELECTROLYTIC CELL:

These electrodes are dipped in and electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation takes place.

Galvanic Cell Vs Electrolytic Cell

Galvanic Cell
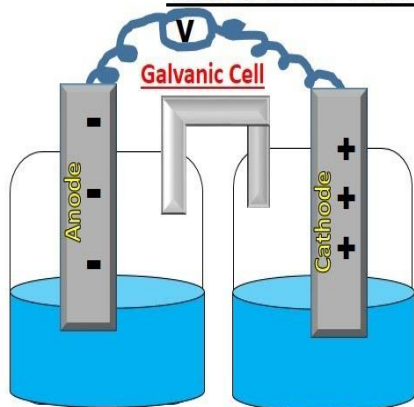
Anode

Cathode

Changes chemical energy into Electrical energy .
1. Anode is –ve
2. Cathode is +ve
3. Spontaneous reaction occurs.
4. Does not require external voltage source.

Battery

Electrolytic Cell

Anode

Cathode

Electrolyte
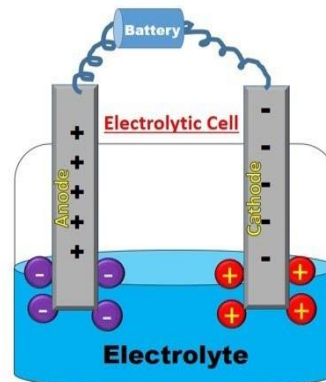
Changes electrical energy into Chemical reaction.
1. Anode is +ve
2. Cathode is -ve
3. Non-Spontaneous reaction occurs.
4. Require external voltage source.

- **ELECTRODE POTENTIAL (E)**

  It may be defined as the tendency of an element, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged. The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.

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

STANDARD ELECTRODE POTENTIAL (E^O)

  It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are :

(i)   1M concentration of each ion in the solution.

(ii)   (ii) A temperature of 298 K.

(iii) (iii) 1 bar pressure for each gas.

- **CELL POTENTIAL OR EMF OF A CELL**
- The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

$$Ecell = E_{cathode} + E_{anode}$$

  For this equation we take oxidation potential of anode and reduction potential of cathode. Since anode is put on left and cathode on right, it follows

  therefore,

$$= ER + EL$$

  For a Daniel cell, therefore ,

$$E^O_{cell} = E^O_{Cu2+ / Cu} = E^O_{Zn / Zn2+} = 0.34 + (0.76) = 1.10V$$

- **CELL DIAGRAM OR REPRESENTATION OF A CELL**

- The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations. The Daniel cell is represented as follows :

$$Zn(s) \mid Zn2+ (C1) \mid\mid Cu2+ (C2) \mid Cu (s)$$

(a) Anode half cell is written on the left hand side while cathode half cell on right hand side.

(b) A single vertical line separates the metal from aqueous solution of its own ions.

$$Zn (s) \mid Zn2+ (aq) ; \qquad Cu2+ (aq) \mid Cu (s)$$
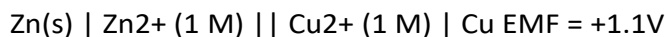**anodic chamber   cathodic chamber**

(c) A double vertical line represents salt bridge

(d) The molar concentration

(C) is placed in brackets after the formula of the corresponding ion.

(e) The value of e.m.f. of the cell is written on the extreme right of the cell. For example,

For example,

Zn(s) | Zn2+ (1 M) || Cu2+ (1 M) | Cu EMF = +1.1V

(f) If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket say for example, when a zinc anode is connected to a hydrogen electrode.
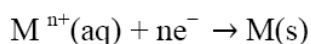
Zn(s)| Zn^{2+} (C_1) || H^+ (C_2) | H_2 | Pt (s)
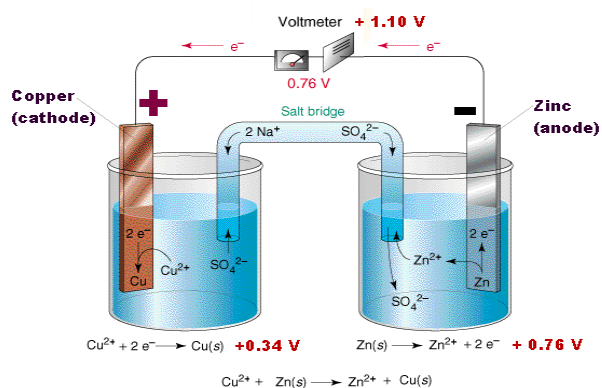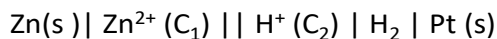
SPONTANEITY OF A REACTION

$\Delta G = - nFE_{CELL}$

- For a spontaneous cell reaction ΔG should be negative and cell potential should be positive.
- If we take standard value of cell potential in the above equation we will obtain standard value of ΔG as well.
- $\Delta G^o = - nFE^o_{CELL}$

The standard electrode reaction can be written as:

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

And Nernst equation can be written as:

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

But the concentration of solid species is taken as unity so the equation turns to:

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

In Daniell cell, the electrode potential for any given concentration Cu^{2+} and Zn^{2+} ion is as follows:

For cathode:

$$E_{(Cu^{2+}/Cu)} = E^\circ_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}]}$$

For anode:

$$E_{(Zn^{2+}/Zn)} = E^\circ_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}]}$$

For cell potential:

$$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$

$$= E(Cu^{2+}/Cu) - E(Zn^{2+}/Zn)$$

$$= \left[E^\circ_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}]} \right] - \left[E^\circ_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}]} \right]$$

$$= \left[E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Zn^{2+}/Zn)} \right] - \frac{RT}{2F} \left[\ln \frac{1}{[Cu^{2+}]} - \ln \frac{1}{[Zn^{2+}]} \right]$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad \dots (1)$$

In this way by knowing the concentration of various species we can calculate the EMF of the cell.

By converting the natural log to base 10 and substituting the value of R, F and T = 298 K, Equation (1) reduces to,

$$E_{cell} = E^\circ_{cell} - \frac{2.303 \, (8.314 \, \text{J/mol K}) \, (298 \, \text{K})}{n \, (96500)} \log_{10} \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= E^\circ_{cell} - \frac{0.059}{n} \log_{10} \frac{[Zn^{2+}]}{[Cu^{2+}]} \dots (2)$$

Equation (2) is more general equation to calculate the EMF of the cell at 298 K. Its value depends on the number of electrons that is being transferred in cell reaction and concentration of ionic species.

Nernst Equation

Nernst gave a relationship between electrode potentials and the concentration of electrolyte solutions known as **Nernst equation**.

For a general electrode reaction,

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

the Nernst equation is

$$E\,(M^{n+} \mid M) = E°(M^{n+} \mid M) - \frac{RT}{nF}\, ln\, \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$E\,(M^{n+} \mid M) = E^{\ominus}\,(M^{n+} \mid M) - \frac{2.303\ RT}{nF}\, log\, \frac{[M(s)]}{[M^{n+}(aq)]}$$

Where E (Mn+|M) = Electrode potential

Eø (Mn+|M) = Standard Electrode potential

R= Gas constant T =Temperature

F = Faraday of electricity, n= Number of electrons gained during the electrode reaction.

Nernst Equation

The standard electrode potentials are measured in their standard states when the concentration of the electrolyte solutions are fixed as 1M and temperature is 298 K. In actual practice electrochemical cells do not have always fixed concentration of the electrolyte solutions. The electrode potentials depend on the concentration of the electrolyte solutions.

[Mn+ (aq)] = Molar concentration of ions

[M] = Molar concentration of metal

Substituting the values of R (8.314 JK-1 mol-1),

T (298 K) and F (96500 coulombs),

the Nernst equation at 25°C becomes

$$E\,(M^{n+}\mid M)\;=\;E^{\circ}(M^{n+}\mid M)-\frac{RT}{nF}\,ln\,\frac{[M(s)]}{[M^{n+}(aq)]}$$

$$E\,(M^{n+}\mid M)\;=\;E^{\ominus}(M^{n+}\mid M)-\frac{2.303\,RT}{nF}\,log\,\frac{[M(s)]}{[M^{n+}(aq)]}$$

$$E\,(M^{n+}\mid M)\;=\;E^{\ominus}(M^{n+}\mid M)-\frac{2.303\times8.314\times298}{n\times96500}\,log\,\frac{[M(s)]}{[M^{n+}(aq)]}$$

$$or\ E\,(M^{n+}\mid M)=\;E^{\ominus}(M^{n+}\mid M)-\frac{0.059}{n}\,log\,\frac{[M(s)]}{[M^{n+}(aq)]}$$

The concentration of the solid phase, [M(s)] is taken to be unity. The above equation may also be written as:

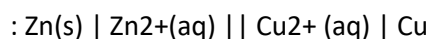$$E\,(M^{n+}\mid M)\;=\;E^{\ominus}(M^{n+}\mid M)-\frac{0.059}{n}\,log\,\frac{1}{[M^{n+}(aq)]}$$

For simplicity, we write this equation as :

$$E\;=\;E^{\ominus}-\frac{0.059}{n}\,log\,\frac{1}{[M^{n+}(aq)]}\quad at\ 25°C.$$

Application Of Nernst Equation

1) Calculation of cell potential using Nernst Equation

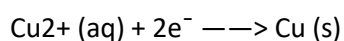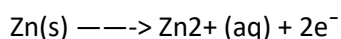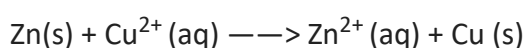Considering a Daniel Cell in which concentration of the solution may not be 1 M.The cell is

: Zn(s) | Zn2+(aq) || Cu2+ (aq) | Cu

 the e..m.f. of the cell is : Ecell = Ecathode− Eanode

= E (Cu2+| Cu) − E (Zn2+ |Zn)

The electrode reactions are :

Zn(s) ——-> Zn2+ (aq) + 2e¯

Cu2+ (aq) + 2e¯ ——> Cu (s)

  The electrochemical cell reaction is:

Zn(s) + Cu^{2+} (aq) ——> Zn^{2+} (aq) + Cu (s)

The electrode potential for the two electrodes can be calculated by using Nernst equation:

$$E \, (Cu^{2+} \mid Cu) = E^{\ominus} \, (Cu^{2+} \mid Cu) - \frac{2.303 \, RT}{2F} \log \frac{[Cu]}{[Cu^{2+}(aq)]}$$

Similarly, electrode potential for zinc electrode,

$$E \, (Zn^{2+} \mid Zn) = E^{\ominus}(Zn^{2+} \mid Zn) - \frac{2.303 \, RT}{2F} \log \frac{[Zn]}{[Zn^{2+}(aq)]}$$

Substituting these values in Eq. (i)

$$E_{cell} = E^{\ominus} \, (Cu^{2+} \mid Cu) - \frac{2.303 \, RT}{2F} \log \frac{[Cu]}{[Cu^{2+}(aq)]}$$

$$- \left[E \, (Zn^{2+} \mid Zn) - \frac{2.303 \, RT}{2F} \log \frac{Zn}{[Zn^{2+}(aq)]} \right]$$

or

$$E_{cell} = E^{\ominus} \, (Cu^{2+} \mid Cu) - E^{\ominus} \, (Zn^{2+} \mid Zn) - \frac{2.303 \, RT}{2F} \log \frac{[Cu][Zn^{2+}(aq)]}{[Cu^{2+}(aq)][Zn]}$$

Now Eø (Cu2+| Cu) – Eø (Zn2+ |Zn) = Eøcell and the concentration of solids is taken as unity so that [Zn] =1 and [Cu]=1

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

or

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]} \text{ at 298 K}$$
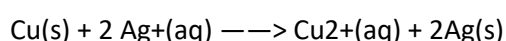
$$\left(\because \frac{2.303 \, RT}{F} = 0.059 \text{ at 298 K} \right)$$

The valencies of zinc and copper are the same i.e. n=2.

Consider an example in which **the valencies of the two metals used in the two half cells are not same.**

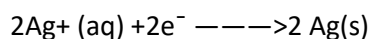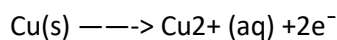Cu| Cu2+(aq) || Ag+(aq) |2Ag(s)

The cell reaction is :

Cu(s) + 2 Ag+(aq) ——> Cu2+(aq) + 2Ag(s)

The EMF of a cell, Ecell = Ecathode– Eanode

Two electrons are released by one copper atom but one electron is accepted by Ag+ according to the reaction.

$Cu(s) ———> Cu2+ (aq) +2e^-$

$2Ag+ (aq) +2e^- ———>2 Ag(s)$

The electrode potential of two electrodes may be written according to Nernst equation as: Electrode potential for silver electrode,

$$E(Cu^{2+} \mid Cu) = E^{\ominus} (Cu^{2+} \mid Cu) - \frac{2.303\ RT}{2F} \log \frac{[Cu]}{[Cu^{2+}(aq)]}$$

Electrode potential for silver electrode,

$$E(Ag^{+} \mid Ag) = E^{\ominus}(Ag^{+} \mid Ag) - \frac{2.303\ RT}{2F} \log \frac{[Ag]^{2}}{[Ag^{+}(aq)]^{2}}$$

It must be remembered that $E^{\circ}(Ag^{+} \mid Ag)$ remains unchanged.
Substituting the values in Eq. (i)

$$E_{cell} = E^{\ominus}(Ag^{+} \mid Ag) - \frac{2.303\ RT}{2F} \log \frac{[Ag]^{2}}{[Ag^{+}(aq)]^{2}}$$

$$- \left\{ E(Cu^{2+} \mid Cu) - \frac{2.303\ RT}{2F} \log \frac{[Cu]}{[Cu^{2+}(aq)]} \right\}$$

or $$E_{cell} = [E^{\ominus}(Ag^{+} \mid Ag) - E^{\ominus}(Cu^{2+} \mid Cu)] - \frac{2.303\ RT}{2F} \log \frac{[Ag]^{2}[Cu^{2+}(aq)]}{[Ag^{+}(aq)]^{2}[Cu]}$$

Now $E^{\ominus}(Ag^{+} \mid Ag) - E^{\ominus}(Cu^{2+} \mid Cu) = E^{\ominus}_{cell}$ and $[Cu] = 1$, $[Ag] = 1$

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

At 298 K, the relation becomes

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

In general, for an electrochemical cell reaction :

$$aA + bB \xrightarrow{\ ne^-\ } cC + dD$$
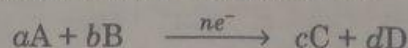
$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^{\ominus}_{cell} - \frac{2.303\ RT}{nF} \log \frac{[C]^{c}\ [D]^{d}}{[A]^{a}\ [B]^{b}}$$

At 298 K, the equation becomes

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.059}{n} \log \frac{[C]^{c}\ [D]^{d}}{[A]^{a}\ [B]^{b}}$$

Some examples of Nernst Equation for cells

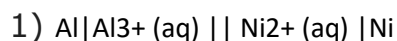1) Al|Al3+ (aq) || Ni2+ (aq) |Ni

The cell reaction is : 2

Al (s) + 3 Ni2+ (aq) ———-> 3 Ni(s) + 2 Al3+ (aq)
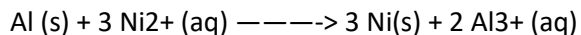
Here n=6

The Nernst equation is :

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.059}{6} \log \frac{[Al^{3+}(aq)]^2}{[Ni^{2+}(aq)]^3} \text{ at 298 K}$$

Electrochemical Cell and Gibbs energy of the Reaction

In electrochemical cells, the chemical energy is converted into electrical energy. The cell potential is related to Gibbs energy change.

In an electrochemical cell, the system does work by transferring electrical energy through an electric circuit.

$\Delta_r G$ = maximum work

For a reaction, occurring in an electrochemical cell whose electrodes differ in a potential by E_{cell} , the work done when amount of charge nF is pushed along by the potential of the cell is given by nFE_{cell} so that

Maximum work = nFE_{cell}

where F is the Faraday constant (the charge on one mole of electrons) and n is the number of moles of electrons transferred in them. When voltaic cell operates, work is done on the surroundings, as electrical energy flows through the external circuit. Such work by convention is taken as negative.

Thus,

$\Delta_r G\phi = w_{max} = -nFE\phi_{cell}$

We use standard cell potential, $E\phi_{cell}$

Therefore

$\Delta_r G\phi = -nFE\phi_{cell}$

where $\Delta_r G\phi$ is the standard Gibbs energy for the reaction.

If the activity of all the reacting species is unity, then $E=E\phi$ and we have

$\Delta_r G\phi = -nFE\phi_{cell}$

Thus, from the measurement of Eø we can calculate an important thermodynamic property. From the temperature dependence of Eø we can also calculate Δ_rHø and Δ_rSø

From the standard Gibbs energy, we can also calculate equilibrium constant by the equation:

Significance

The above equation helps us to predict the feasibility of the cell reaction. For a cell reaction to be spontaneous, Δ_rG must be negative. This means that E must be positive for a spontaneous cell reaction.

SOLUBILITY EQUILIBRIUM

- Solubility refers to the ability of a substance to dissolve. In the study of solubility equilibrium we generally deal with low solubility compounds (those which dissolve poorly)
- Low solubility compounds are classified as precipitates. A set of solubility rules indicate which combination of ions generally form precipitates. These rules allow us to identify low solubility substances and potential precipitates. The concentrations of the ions present however are the final determiners of precipitate formation.

Ksp AND SOLUBILITY

- Since solubility is an equilibrium phenomena, equilibrium concepts can readily be applied.
- If the system is at equilibrium, the solution must be saturated (no more solid can be dissolved). Equilibrium concepts cannot be applied to unsaturated solutions (more solid can still be dissolved) since equilibrium has not yet been reached.
- For a typical saturated solution of silver chloride,

    $AgCl_{(s)} \longleftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$

    the equilibrium expression is:

    $K = [Ag^+] \times [Cl^-] / 1$ or simply $[Ag^+] \times [Cl^-]$

    Since AgCl is and solid it is not included in the equilibrium expression!

- This K value is called the K_{sp}. "sp" stands for solubility product. The product of the concentrations of the soluble ions.

Hard and Soft Acids and Bases.

Pearson's Principle of Hard and Soft Acids and Bases (HSAB) can be stated as follows:

Hard Acids prefer to bond with Hard Bases, and Soft Acids prefer to bond with Soft Bases.

➢ However this very simple concept was used by Pearson to rationalize a variety of chemical information.

➢ 1983 – the qualitative definition of HSAB was converted to a quantitative one by using the idea of *polarizability*. A less polarizable atom or ion is "hard" and a more easily polarized atom or ion is "soft".

Hard acid   : High positive charge
                          Small size
                          Not easily polarizable

Hard base   : Low polarizability
                          High electronegativity
                          Not easily oxidized

Soft acid   : Low positive charge
                          Large size; easily oxidized
                          Highly polarizable

Soft base   : High polarizability
                          Diffuse donor orbital
                          Low electronegativity
                          Easily oxidized

Hard Acids	Borderline Acids	Soft Acids
H^+, Li^+, Na^+, K^+		
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^2		
BF_3, BCl_3, $B(OR)_3$	$B(CH_3)_3$	BH_3, Tl^+, $Tl(CH_3)_3$
Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3		
Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+}	Cu^+, Ag^+, Au^+, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, CH_3Hg^+, $[Co(CN)_5]^{3-}$, Pd^{2+}, Pt^{2+}, Pt^{4+},
Ions with formal oxidation states of 4 or higher		Br_2, I_2
HX (hydrogen-bonding molecules)		Metals with zero oxidation state π acceptors: e.g.,

e.g. *although all alkali metals in ionic form M⁺ are "hard", the larger, more polarizable, Cs⁺ ion is much softer than Li⁺*

- also N: compounds are not all equal

H₃N: versus pyridine

pyridine is much more polarizable.

Hard Bases	Borderline Bases	Soft Bases
		H^-
F^-, Cl^-	Br^-	I^-
H_2O, OH^-, O^{2-}		H_2S, SH^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	PR_3, $P(OR)_3$, AsR_3, C_2H_4, C_6H_6

Corrosion

When metals are exposed to atmospheric conditions, they react with air or water in the environment to form undesirable compounds (usually oxides). This process is called corrosion.

The least active metals such as gold, platinum and palladium are attacked by environment.

For example: Silver tarnishes, copper develops a green coating, lead or stainless steel lose their lustre due to corrosion.

Corrosion is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.

In case of iron, corrosion is called **rusting.** Chemically rust is hydrated form of ferric oxide, $Fe_2O_3 \cdot xH_2O$. Rusting of iron is generally caused by moisture, carbon dioxide and oxygen present in air.

Rusting takes place only when iron is in contact with moist air.

Wet and Dry Corrosion

There are several types of corrosion, including wet corrosion and dry corrosion.

Dry corrosion occurs when there is no water or moisture to aid the corrosion, and the metal oxidises with the atmosphere alone.

Wet corrosion of metals occurs through electron transfer, involving two processes, oxidation and reduction. In oxidation, the metal atoms lose electrons. The surrounding environment then gains the electrons in reduction. The metal, where electrons are lost, is called the anode. The other metal, liquid or gas which gains the electrons is called the cathode.

Corrosive Environments

As mentioned previously, most corrosion is the formation of metal oxides. This means that any metal (with the exception of gold) will oxidise in any environment that contains oxygen.
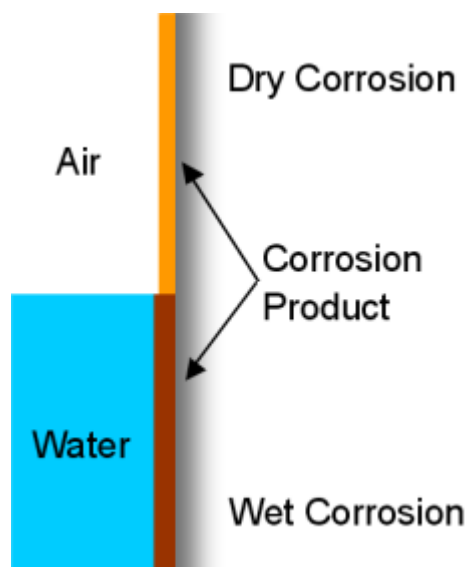
Air contains, on average, 21% oxygen, 78% nitrogen, and 1% argon. It can also contain water vapour, ozone, and carbon dioxide.

Water is very commonly aerated which again means there is oxygen for reaction with metals.

There are many factors that dictate how corrosive an environment is. One is the amount of oxygen available to form corrosion products or the presence of water or moisture which greatly accelerate the rate of corrosion. Another is the presence of other elements, ions and compounds that can limit or enhance corrosion rates. Therefore corrosion rates are often considered in different atmospheres: industrial, rural and marine. Each of these environments will contain different amounts of oxygen and other "pollutants" like ozone, salt, dusts, sulphur dioxide, ammonia, hydrogen and hydrogen sulphide.

1: Dry Corrosion

Dry corrosion or oxidation occurs when oxygen in the air reacts with metal without the presence of a liquid.
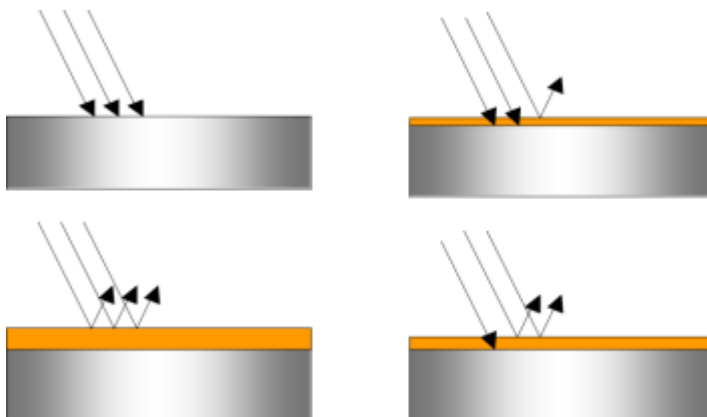
Typically, dry corrosion is not as detrimental as wet corrosion, but it is very sensitive to temperature. If you hold a piece of clean iron in a flame, you will soon see the formation of an oxide layer!

Most engineering metals have a slow oxidation rate in the atmosphere at ambient temperature.

The differences in the rate of dry corrosion vary from metal to metal as a result of the mechanisms involved.

n dry corrosion the oxygen has to be able to make contact with the metal surface.

Initially this is not a problem, but as soon as corrosion starts to occur the oxide layer, that forms on the metal surface, will limit the amount of oxygen that can further react with the metal.

i) Oxidation Corrosion

$$2M \longrightarrow 2M^{n+} + 2ne^- \qquad \text{(oxidation)}$$
$$n/2O_2 + 2ne^- \longrightarrow nO^{2-} \qquad \text{(reduction)}$$
$$\underline{2M + n/2O_2 \longrightarrow 2M^{n+} + nO^{2-}}$$

Metal oxide

The metal loses electrons to form an ion and some free electrons. The ionic metal can then react with oxygen to form a metal oxide. In dry corrosion, the oxygen comes from the air, in wet corrosion, the oxygen is supplied by aerated water.

Not all oxide layers that form on metals are protective. If the oxide does not form a continuous layer on the surface of the metal, it will not be able to reduce the amount of oxygen reaching the metal surface.

 If the metal forms an oxide whose area is less than the area of the metal then the surface will show gaps in the protective layer.

If the metal forms an oxide whose area is greater than the area of the metal then the surface will show blistering and flaking of the protective layer.

Only if the area of the oxide that forms is the same as the area of the metal will the oxide layer protect the metal from further corrosion

2: Formation of an Oxide Layer

The difference in oxidation rates depends on the conductivity of the oxides because the ions have to move through the oxide layer.
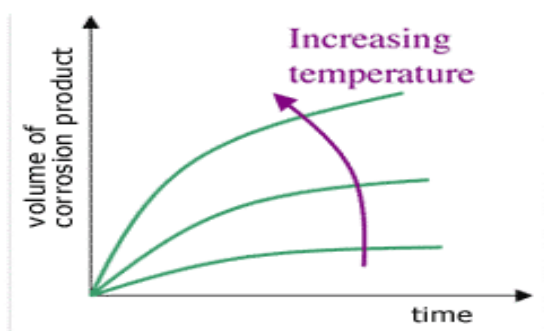

Oxidation occurs much more rapidly as temperature increases because the mobility of ions within the oxide layer increases.

 In some cases, dry corrosion is actually encouraged. The formation of an oxide layer on the surface of a metal will, in some instances, lead to a reduction in the rate of corrosion.

When a metal oxidises and forms an outer layer, this layer can remain on the surface of the smetal and limit further corrosion by inhibiting the ability of oxygen or other corrodents to reach the metal surface. This is known as passivation.

3: Passivation

Passivation of a metal surface through the formation of an oxide layer is found in many common metals and alloys. Aluminium naturally forms a protective oxide layer (or scale) which slows down further oxidation and corrosion. Stainless steel has chromium added to it, which forms a very protective oxide layer that prevents further corrosion.
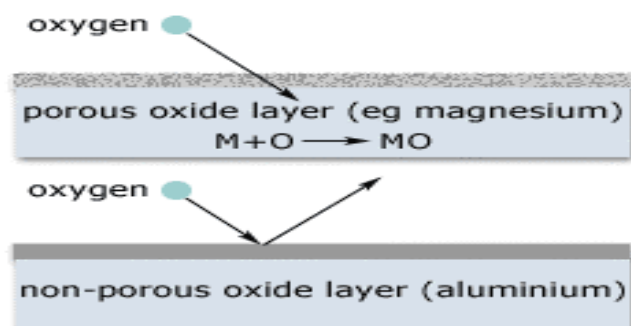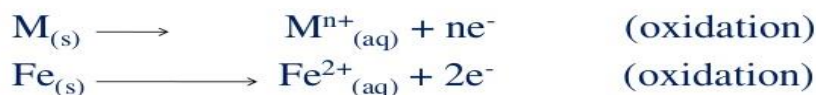

Wet or electrochemical corrosion (Electrochemical theory)

Two essential requirements are:

i) Formation of anodic and cathodic areas

ii) Electrical contact between the cathodic and anodic parts to enable the conduction of electrons

Mechanism

i)Anodic reactions

$$M_{(s)} \longrightarrow M^{n+}_{(aq)} + ne^- \qquad \text{(oxidation)}$$

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^- \qquad \text{(oxidation)}$$

ii) Cathodic reactions

a) In acidic solution in the absence of O_2

$$2H^+ + 2e^- \longrightarrow H_2$$

b) In acidic solution in the presence of O_2

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

c) In neutral or alkaline medium in the absence of O_2

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

d) In neutral or alkaline medium in the presence of O_2

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

(e)In neutral or alkaline medium in the presence of O_2

$$O_2 + 2H_2O + 4e- \longrightarrow 4OH-$$

(such type of corrosion involving O_2 is called oxygen type corrosion)

Fig. 5.3 Small Anodic area and large Cathodic area
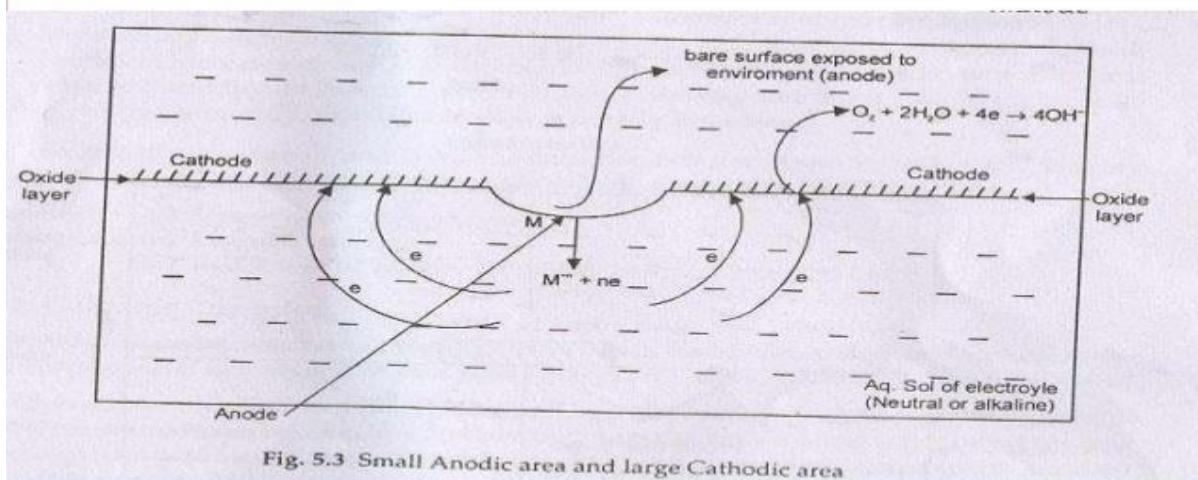
e.g. *Rusting of iron occurs by O_2 in the presence of aqueous solution*

At anode $\qquad$ $Fe \longrightarrow Fe^2+ 2e^-$

At cathode $\qquad$ $1/2O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Overall reaction $\quad$ $Fe + 1/2O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^-$ or $Fe(OH)_2$

| Wet corrosion	Dry corrosion
Occursin presence of water or an electrolyte.	occurs in absence of liquid or electrolyte.
It is an electrochemical attack.	It is a chemical attack.
Occurs at low temperature.	occurs e at high temperature.
low temperature corrosion	high temperature corrosion.
It is generally fast.	It is generally slow.
Eg. Rusting of iron in water.	Eg. Attack of steel furnace by gases at high temperature.

TYPES OF WET CORROSION

1. Galvanic Corrosion /Bimetallic corrosion/ Differential metal corrosion

E.g. Zinc and copper couple

More reactive $Zn \longrightarrow Zn^{2+} + 2e^-$ At anode
(Corrodes)

Less reactive $Cu + 2e^- \longrightarrow Cu$ At Cathode
(protected) no reaction takes place

Fig. 5.7 Galvanic Corrosion
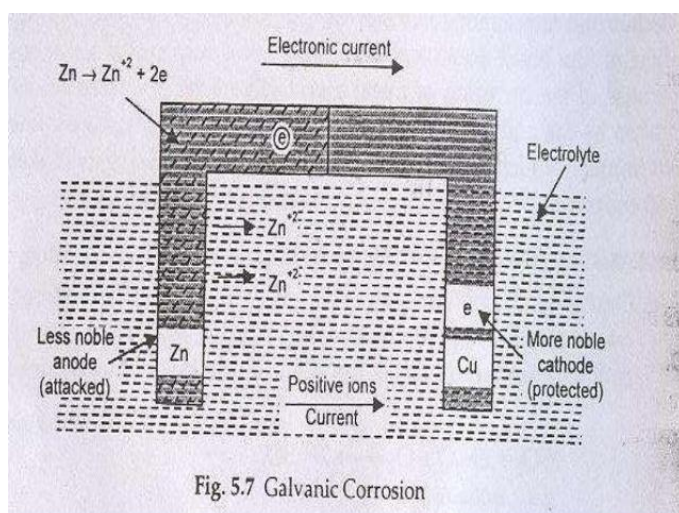
The **Pilling–Bedworth** ratio (P–B ratio), in corrosion of metals, is the ratio of the volume of the elementary cell of a metal oxide to the volume of the elementary cell of the corresponding metal (from which the oxide is created)

Poubaix 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.

Oxidizing conditions are described by the top part of the diagram (high positive electrode potential).
Reducing conditions are described by the bottom part of the
diagram (high negative electrode potential). Acidic solutions are
presented in the left side of the diagram (PH lower than 6).
Alkaline solutions are presented in the right side of the diagram (PH higher than 6).

The lines of the diagrams dividing different zones of the equilibrium states are calculated by the Nernst equation:

$$E = E^0 - (0.059/n)*\ln C_{ion}$$

Where:

E^0 - Standard electrode potential, V;
n - number of electrons transferred;
C_{ion} - molar activity (concentration) of ions.

Pourbaix diagrams allow to determine the corrosion behavior of a metal in water solutions i.e. the direction of electro-chemical processes and the equilibrium state of the metal at a certain electrode potential in a water solution at a certain value of PH. Normally the Poubaix diagrams are built for the water solutions with the concentrations of metal ions 10^{-6}M and at the temperature 298K (77ºF/25ºC).

Horizontal lines of the Poubaix diagrams correspond to the redox reactions, which are independent of PH.

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

Diagonal lines of the Poubaix diagrams correspond to the redox reactions, which are dependent on PH.
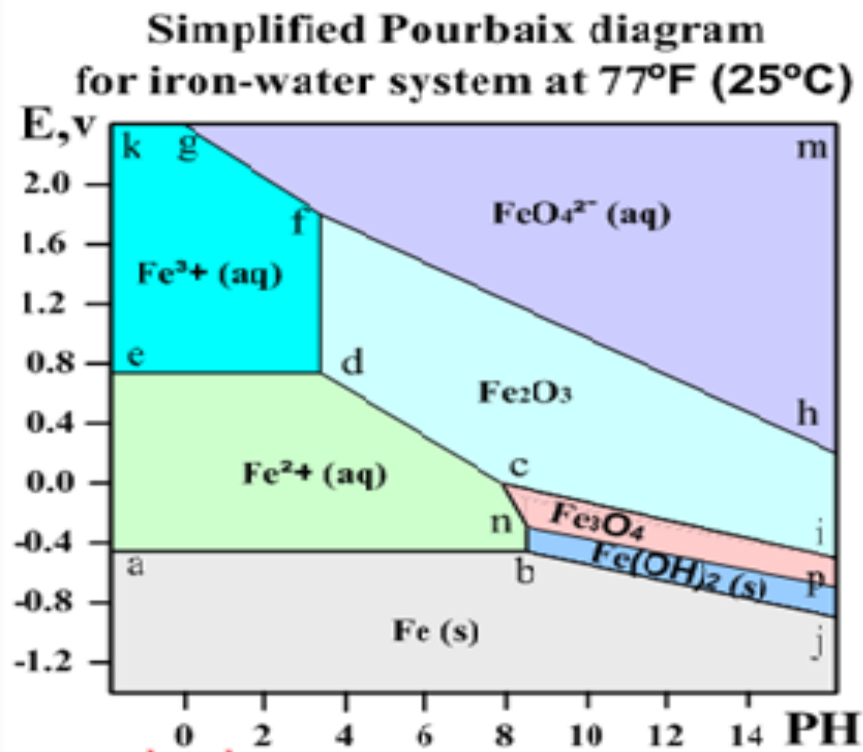
An example of a Pourbaix diagram for the system iron-water is presented in the picture.

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 Fe2+ (**corrosion zone**). Metallic iron oxidizes in this zone.

- **e-d-f-g-k**: Aqueous solution of ion Fe3+ (**corrosion zone**). Metallic iron oxidizes (corrodes) in this zone.

- **h-f-g-m**: Aqueous solution of ion FeO 2- (**corrosion zone**).
  ~4~

- **c-d-f-h-i**: Solid ferrous oxide Fe2O3 (**passivation zone**). Iron oxidizes (corrodes) in this zone however the resulted oxide film depresses 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 Fe3O4 (Fe2O3*FeO) (**passivation zone**). The oxide film causes passivation.

- **b-n-p-j**: Solid hydroxide (II) Fe(OH)2 / FeO*nH2O / green rust (**passivation zone**).

Here are some of the reactions and the corresponding lines of the Fe-H2O Pourbaix diagram:

- **a-b: Fe(s) = Fe2+(aq) + 2e-** Redox reaction independent of PH. The equilibrium occurs at the electrode potential value -0.44V, which is equal to the s tandard electrode potential of iron (see the E lectrochemical series).

- **e-d: Fe2+(aq) = Fe3+(aq) + e-** Redox reaction independent of PH.

- **d-f: 2Fe3+(aq) + 3O2- = Fe2O3(s)** Non-redox reaction dependent on PH.

- **b-n: Fe2+(aq) + 2OH-(aq) = Fe(OH)2(s)** Non-redox reaction dependent on PH.

- **c-d: 2Fe2+(aq) + 3H2O = Fe2O3(s) + 6H+(aq) +2e-** Redox reaction dependent on PH.

- **b-j: Fe(s) + 2OH-(aq) = Fe(OH)2(s) + 2e-** Redox reaction dependent on PH.

Limitations of Pourbaix diagrams:

- The diagrams provide no information about the kinetic parameters of the corrosion reactions.

- The diagrams consider pure metals and aqueous solutions at standard conditions (temperature 298K, pressure 1 bar, ion concentration 10-6M). Thermodynamic conditions of corrosion for a lloys and for non-standard conditions differ from those described by Pourbaix diagrams.

- The diagram do not take into account non-ideal behavior of aqueous solutions. Some thermodynamic data used for building diagrams are not precise enough.